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THE JOURNAL OF SOIL SCIENCE

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VOLUME 5 NUMBER 2
JULY 1954

OXFORD
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THE
JOURNAL OF SOIL SCIENCE

Editor: G. V. JACKS, M.A.

COMMONWEALTH BUREAU OF SOIL SCIENCE
ROTHAMSTED EXPERIMENTAL STATION, HARPENDEN, HERTS.

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A CHRONOSEQUENCE OF SOILS AND VEGETATION NEAR MOUNT SHASTA, CALIFORNIA

III. SOME PROPERTIES OF THE MINERAL SOILS

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(*University of California*)

Introduction

In the first two papers of this series (Dickson and Crocker, 1953*a*, 1953*b*) it was established that the characteristic differences of five soil-vegetation systems, developed on a group of mudflows near Mount Shasta, were mainly dependent upon their time states. It was considered that the ecosystem-determining factors (climate, organisms, topography, and parent material) were essentially the same for all five members of the sequence. On this basis, the changes in vegetation (plant succession), the development of the forest floor, and the development of the organic carbon and nitrogen profiles were described as functions of time. In this paper it is proposed to examine some additional properties of the mineral soils and to show their relationship to changes in the vegetation, forest floor, and the organic profile.

Methods

The five soil profiles were carefully selected in the field so as to eliminate unnecessary variations in the ecosystem-determining factors wherever this was possible. The samples were taken directly beneath the sites chosen for the forest-floor samples, as reported in a previous paper. Five samples were taken from each profile, representing the following depths: 0–2½, 2½–5, 5–12, 12–24, 24–36 in. All analyses, except where otherwise specified, refer to the fine earth fraction. Apparent density samples were taken by means of a Uhland sampling tool. The apparent densities were used to compute amounts of exchangeable bases per profile (volume basis) for graphical purposes, and these are expressed in milliequivalents per 0·05 sq. ft. to a depth of 36 in. In the case of depth functions, they are expressed as milliequivalents per 0·01 cu. ft.

Results

Apparent density

The apparent density (bulk density) for each sample is given in Table 1. From these figures the apparent density of the 36-in. profile was computed and plotted as a function of time (Fig. 1). This curve is compared to the values obtained for parent material samples.

The phenomenal change, which occurred in the 27- to 60-year period, is logically related to the large deposit of pine-leaf litter which occurred in this period and to the increase in the number of plant roots. The lack of further change in the period which followed is roughly coincident with a reduced accumulation rate of soil organic matter (Dickson and Crocker,

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1953*b*), attributable perhaps to a higher rate of loss for the system, during this time.

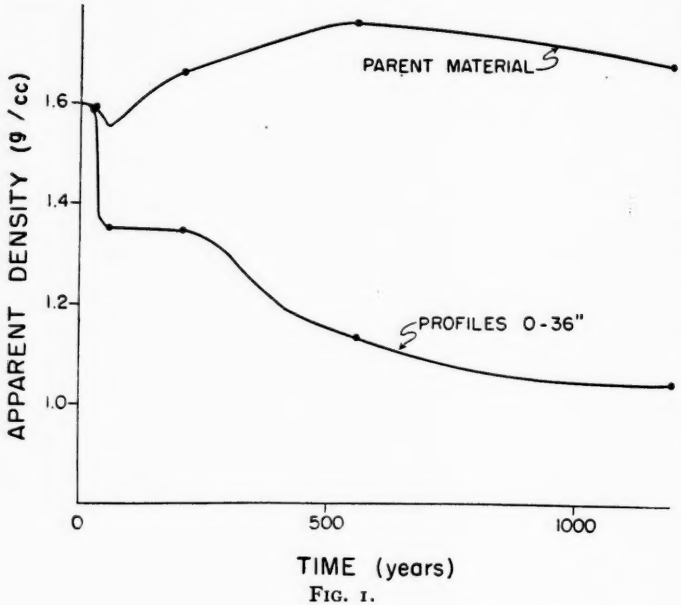

FIG. 1.

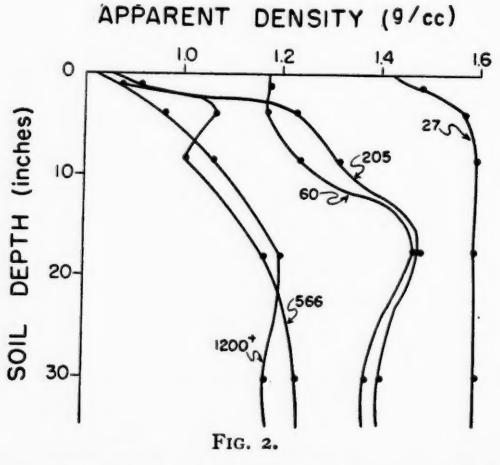

FIG. 2.

The depth functions (Fig. 2) show that the processes affecting apparent density were more effective at the surface and became extended downward as time advanced. The values in the surface 2½ in. were reduced from 1·6 g./c.c. to as low as 0·88 g./c.c. If the apparent density values

are plotted against per cent. organic carbon, a fairly close relationship is obtained in which the apparent density decreases by 0·45 g./c.c. as carbon increases from zero to 1 per cent. and then decreases by only 0·27 g./c.c. as carbon increases from 1 to 5·65 per cent.

TABLE 1

Composition of Soil Samples

Depth (in.)	*Soil*		*Colour 10 YR.*	*'Free' iron oxide (as Fe)%*	*Apparent density (g./c.c.)*	*Fine earth < 2 mm. (%)*
	Age (years)	*pH*				
0–2½	27	5·82	6/1	0·072	1·48	82
	60	5·49	4/1	0·108	1·18	93
	205	5·72	3/1	0·081	0·88	90
	566	6·08	3/3	0·149	0·92	67
	1,200+	6·25	3/3	0·177	0·88	70
2½–5	27	5·99	7/1	0·086	1·57	79
	60	5·98	5/1·5	0·111	1·17	93
	205	5·74	4/1	0·090	1·23	91
	566	6·20	4/2	0·168	1·07	60
	1,200+	6·20	4/2	0·209	0·96	74
5–12	27	6·10	7/1	0·079	1·60	75
	60	6·10	6/2	0·116	1·23	86
	205	5·66	5·5/2	0·094	1·31	87
	566	6·15	5/3	0·178	1·00	64
	1,200+	6·32	5/3	0·216	1·06	71
12–24	27	6·10	7/1	0·089	1·59	75
	60	6·20	7/1	0·096	1·47	84
	205	6·60	7/2	0·088	1·48	90
	566	6·35	7/3	0·178	1·16	66
	1,200+	6·52	7/3	0·172	1·20	64
24–36	27	6·20	7/1	0·089	1·60	63
	60	6·18	7/1·5	0·103	1·37	94
	205	6·54	7/2	0·106	1·40	89
	566	6·32	7/3	0·161	1·23	60
	1,200+	6·57	7·3	0·206	1·17	55

Changes in pH

As soon as litter was deposited on the surface of the mudflows, a pH gradient was set up in the system. At first this consisted of an abrupt change from pH 4·2–4·5 (litter) to pH 6·2–6·5 (parent material). The forest floor soon became differentiated into two layers having pH 4·2–4·5 (L), and pH 4·6–5·2 (F), but the pH trend in the mineral soil was somewhat more elaborate (Fig. 3).

The pH of the surface 2½ in. rapidly dropped to a minimum of 5·5 at the 60-year point. The pH values of the 2½–5 and 5–12-in. layers were also reduced, but did not reach their minima until later. This lag phenomenon appears to be related in some way to the downward movement of organic matter. The pH, however, was not related to the *quantity* of organic matter, nor was it related to any of the other properties measured, including the exchangeable cations. The increase in pH of the subsoil at the 205-year point might have been due to the leaching of bases from the heavy deposit of litter prior to this time.

Soil colour

All of the samples were covered fairly closely by the 10 YR colour chart (Munsell colour chips). It was found that the colour *value* changed greatly (from 7 to 3) with respect to both time and depth (Fig. 4). Colour designations are indicated at various points along the *value* time functions. The colour *chroma* developed with time (from 1 to 3), but did not vary much with depth.

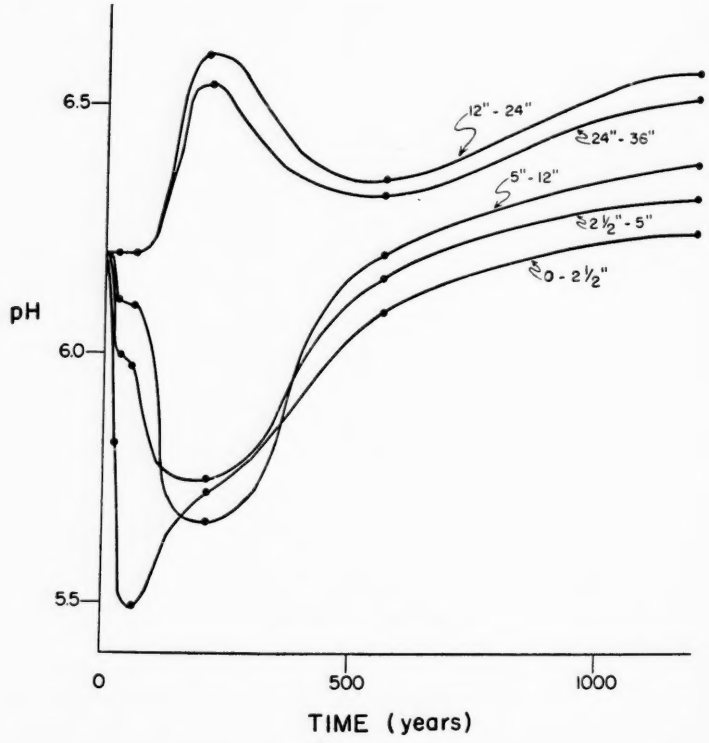

FIG. 3.

Treatment of the soils with hydrogen peroxide changed the colour *values* to nearly 7 in all cases, suggesting that modification of this property with time was mainly related to organic matter. Removal of the free iron oxide by the method of Deb (1950) changed the colour *chroma* to approximately 1 in all cases, suggesting that the change in chroma with time was due to free iron oxide coatings on the soil particles.

Free iron oxide

The free iron oxide was extracted by means of a dilute $Na_2S_2O_4 . 2H_2O$ solution as recommended by Deb (1950). The quantities of iron thus

obtained were unexpectedly small (0·1 to 0·2 per cent. Fe) in view of the colours of the samples. There were no iron concretions observed in the profiles.

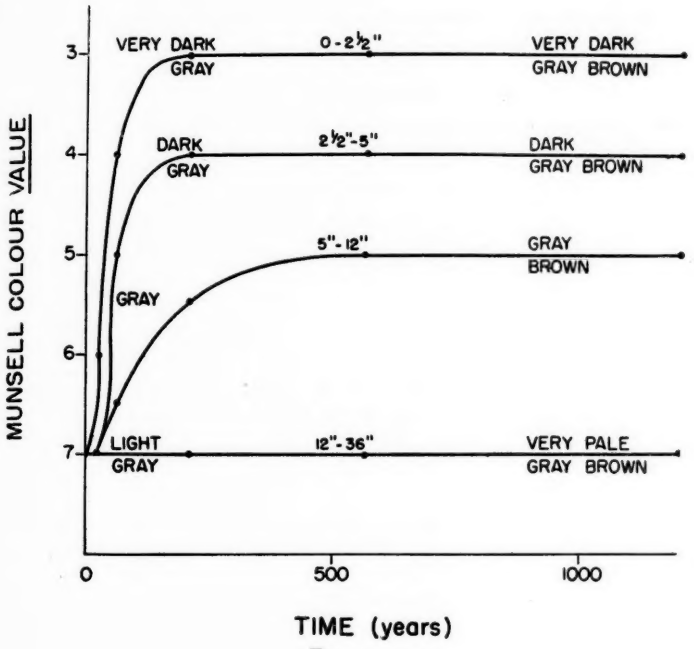

FIG. 4.

The values obtained for the three younger soils and the parent material lay between the limits 0·072 per cent. and 0·116 per cent. Fe, and the variations showed no particular relation to time. The 566-year soil, however, had values lying in the range 0·149 to 0·178 per cent. Fe, while those of the oldest soil varied from 0·172 to 0·216 per cent. Fe. It thus appears that the slight iron oxide accumulation did not occur until after the 205-year mark, and, in this respect, differed from all other properties observed in these soils, except the development of colour *chroma*.

There were no obvious horizons of accumulation within the two older soils.

Soil moisture characteristics

The moisture contents of the soil samples were determined by oven-drying (110° C.) when in equilibrium with (*a*) the laboratory atmosphere (air dry), (*b*) 15-atmosphere tension in a standard pressure membrane apparatus, and (*c*) moisture equivalent tension in a standard moisture equivalent centrifuge. The resulting data are given in Table 2. For

graphical purposes the results were calculated into terms of grammes of water per 36-in. profile, as previously described, and the results are shown in Figs. 5, 6, and 7.

Several points of interest are observable in these data. As might be expected from the coarse sandy nature of the soils, the moisture values

TABLE 2

Water Contents (%, Dry Basis)

Soil depth (in.)	*Soil age (years)*	*Moisture equivalent*	*15-atmosphere percentage*	*Air-dry soil*	*'Available* water'*
0–2½	27	5·54	1·44	0·55	4·10
	60	12·07	3·95	1·51	8·12
	205	15·90	6·78	2·29	9·12
	566	20·60	8·20	4·30	12·40
	1,200+	19·60	8·08	4·31	11·52
2½–5	27	5·88	1·33	0·53	4·55
	60	9·21	2·74	1·13	6·47
	205	9·27	3·33	1·25	5·94
	566	16·50	6·20	3·68	10·30
	1,200+	18·20	9·50	4·37	8·70
5–12	27	5·37	1·16	0·52	4·21
	60	8·62	2·22	0·98	6·40
	205	7·64	2·30	1·09	5·34
	566	14·80	6·01	3·54	8·79
	1,200+	17·10	7·79	4·26	9·31
12–24	27	5·80	1·31	0·53	4·49
	60	6·69	1·67	0·70	5·02
	205	5·10	1·35	0·47	3·75
	566	13·70	5·16	2·85	8·54
	1,200+	13·40	6·43	3·22	6·97
24–36	27	7·10	1·42	0·64	5·68
	60	7·78	1·72	0·60	6·06
	205	6·92	1·84	0·55	5·08
	566	12·40	4·41	2·36	7·99
	1,200+	14·60	7·59	3·69	7·01

* Difference between M.E. and 15-atmosphere percentage.

are all comparatively low. The moisture content in all three states increase with time and decrease with soil depth, showing a general relation to the development of the organic profile and related properties. It is perhaps significant that the air-dry state (after some months in the laboratory) had a lower water content than the 15-atmosphere state, believed by soil physicists to approximate the permanent wilting percentage. The figures given in Table 2, in per cent. by weight, indicate that the so-called 'available water' increased with time. However, when converted to a soil-volume basis (Fig. 5) the values are very similar: 230, 307, 253, 265, and 231 g. available water per 36-in. profile, youngest to oldest respectively. The irregularities in the moisture equivalent and available moisture curves (Fig. 5) are believed to be largely due to variation in the particle size distribution of the sand fraction; this causes, for

example, the moisture equivalent values for the 205-year soil to appear unduly low in the subsoil (Fig. 6). It was expected that both the 60-year and 205-year soils would have the greater amounts of available water because of their lower >2 mm. fraction.

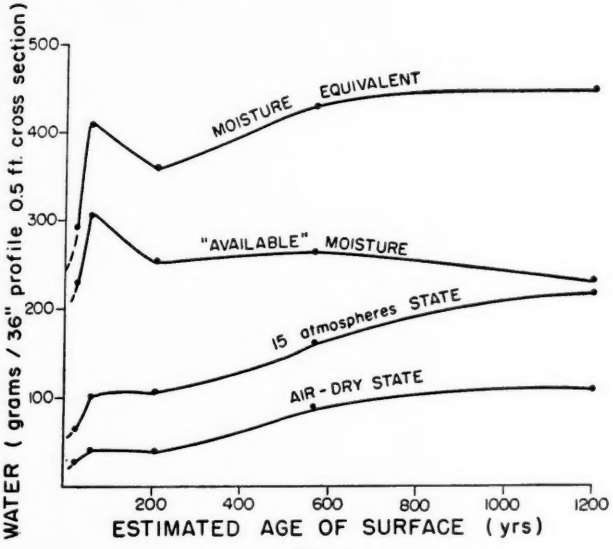

FIG. 5.

The increase in the moisture equivalent from 6 per cent. in the youngest soil to more than 20 per cent. in the uppermost horizons of the two older soils, while rather obviously related to the development of the organic profile, is probably significantly influenced by contemporaneous changes. Of these the reorientation and organization of the mineral particles in new structural arrangements are undoubtedly significant. Such effects, however, are so intimately bound up with the organic phase that their separation and further elucidation are not possible here.

It is difficult to evaluate the moisture properties in terms of vegetation growth and succession and hence of soil development. It may well be, however, that the increase in the 15-atmosphere percentage with time, assuming that this approximates the wilting-point, is perhaps the most important aspect of the water constants with respect to changes in the vegetative assemblage. It should be recalled from an earlier paper that, during most of the summer period, the soils were observed to be very dry (possibly air-dry) to considerable depths.

Base exchange data

The cation exchange capacity of the whole soil was determined by the neutral normal ammonium acetate method (A.O.A.C., 1940) and the exchangeable bases were determined in the extract. These data, in terms of milliequivalents per hundred grammes are given in Table 3.

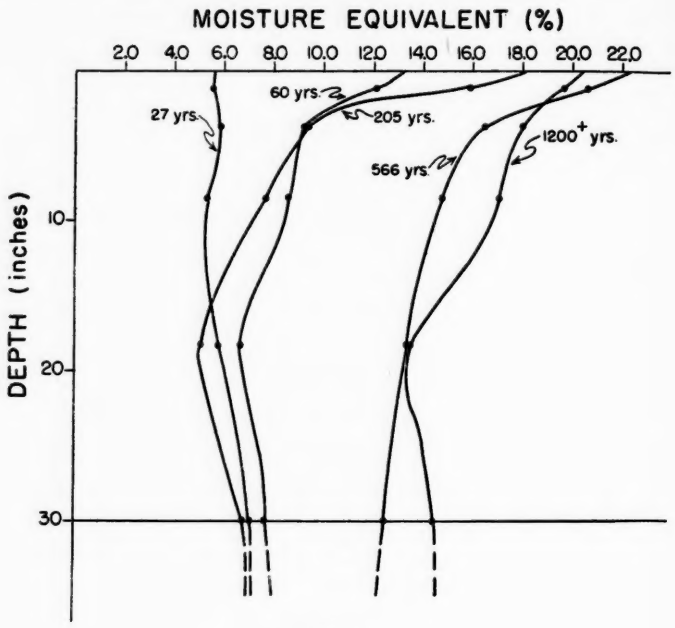
MOISTURE EQUIVALENT (%)
2.0 4.0 6.0 8.0 10.0 12.0 14.0 16.0 18.0 20.0 22.0
DEPTH (inches)
10
20
30
27 yrs.
60 yrs.
205 yrs.
566 yrs.
1200+ yrs.

FIG. 6.

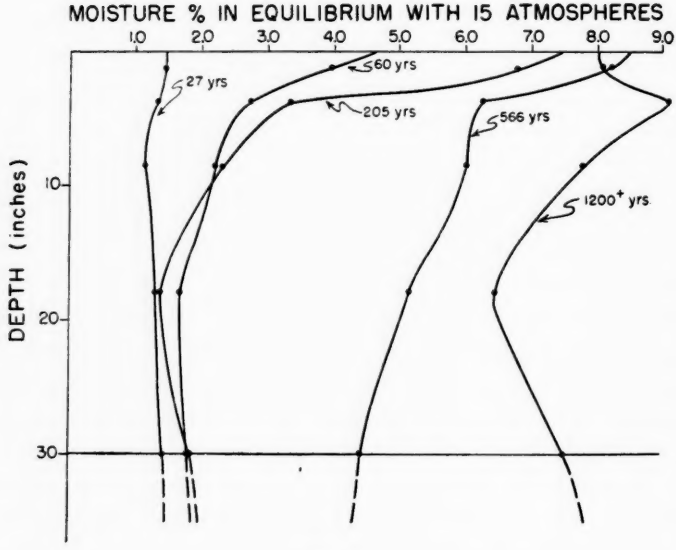
MOISTURE % IN EQUILIBRIUM WITH 15 ATMOSPHERES
1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0
DEPTH (inches)
10
20
30
27 yrs
60 yrs
205 yrs
566 yrs
1200+ yrs

FIG. 7.

The calcium and magnesium were determined by A.O.A.C. (1940) methods and sodium and potassium were determined by means of a Beckman flame photometer. The exchangeable hydrogen was determined by difference. For graphical purposes the data were calculated as milliequivalents per profile or per unit volume in the manner previously explained.

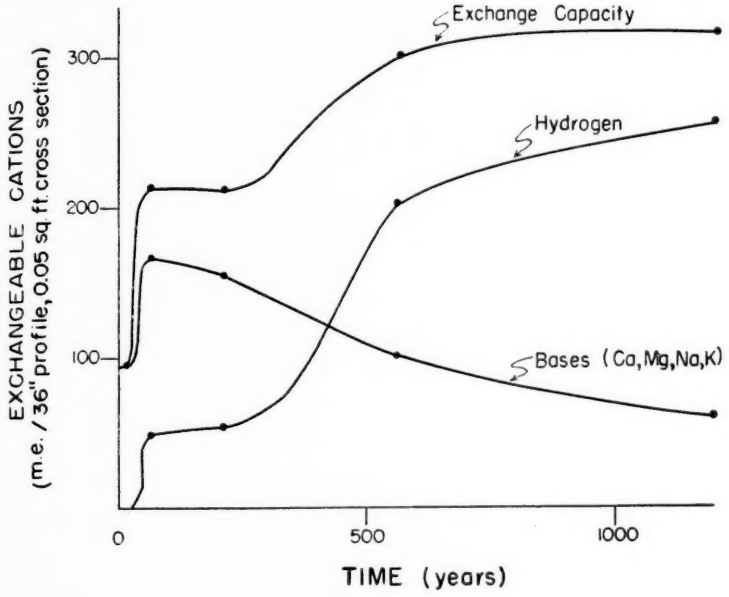

FIG. 8.

Exchangeable hydrogen was also determined by direct methods for most of the soils, using both the meta-nitrophenol method (Piper, 1944) and an unpublished method of Barshad. The direct determinations indicated that the exchangeable hydrogen as determined by the difference between the ammonium exchange capacity and the total ammonium replaced cations is too low. Exploratory tests also revealed that the barium exchange capacities were higher than the ammonium exchange capacities. However, inasmuch as these analyses did not affect any of the general conclusions with respect to developmental trends and affected only questions of magnitude, it was decided to adhere to the more frequently used methods. The exchangeable hydrogen, for example, whether determined directly or by difference, still showed no correlation with pH measurements, as reported elsewhere in this paper.

The exchange capacity of the soil, expressed in milliequivalents per 36-in. profile (Fig. 8), increased rapidly during the 27- to 60-year period, increased only very slightly in the 60- to 205-year period, and then rose approximately 50 per cent. farther in the two oldest members. The

striking similarity of this function to those for carbon and nitrogen indicated that the development of exchange capacity was closely related to the accumulation of organic matter.

TABLE 3

Base Exchange Data (m.e./100 g.)

Depth (in.)	*Age (years)*	*Capacity*	*Calcium*	*Magnesium*	*Sodium*	*Potassium*	*Hydrogen*
0–2½	27	1·92	1·16	0·29	0·11	0·10	0·26
	60	14·56	5·86	1·12	0·12	0·25	7·21
	205	17·30	8·26	1·74	0·05	0·53	6·72
	566	20·50	8·34	0·59	0·17	0·36	11·04
	1,200+	19·80	4·84	0·60	0·11	0·18	14·07
2½–5	27	2·00	1·22	0·64	0·11	0·10	0·00
	60	6·69	3·68	0·60	0·12	0·18	2·11
	205	9·35	3·80	0·52	0·21	0·44	4·38
	566	14·75	4·20	0·32	0·16	0·24	9·83
	1,200+	16·50	2·30	0·26	0·17	0·09	13·68
5–12	27	2·00	1·28	0·64	0·14	0·07	0·00
	60	5·35	2·88	0·66	0·14	0·16	1·51
	205	5·43	1·90	0·78	0·21	0·26	2·28
	566	10·80	2·38	0·48	0·15	0·18	7·61
	1,200+	12·20	1·20	0·52	0·14	0·05	10·29
12–24	27	2·00	1·30	0·50	0·12	0·08	0·00
	60	2·51	1·65	0·48	0·12	0·14	0·12
	205	2·00	1·14	0·40	0·16	0·18	0·12
	566	8·20	1·71	0·40	0·14	0·16	5·79
	1,200+	8·20	1·13	0·22	0·12	0·04	6·69
24–36	27	2·09	1·34	0·64	0·14	0·08	0·00
	60	2·93	1·98	0·50	0·15	0·16	0·14
	205	2·84	1·88	0·48	0·17	0·27	0·04
	566	8·70	2·18	0·48	0·14	0·14	5·76
	1,200+	9·03	1·18	0·34	0·15	0·04	7·32

The relation between organic matter and exchange capacity is further exemplified by the similarity of the depth functions. The characteristic of the depth functions (Fig. 9) was to diminish gradually with depth from a high value at the surface. Although there was no pronounced zone of accumulation in the subsoil, the values for the 24–36-in. layer were somewhat higher than might be expected, and may be indicative of such a development far into the future.

In Fig. 8 the exchange capacity is also compared with the total exchangeable bases (Ca, Mg, Na, K) and with exchangeable hydrogen. The significant result is that the total exchangeable bases per 36-in. profile of the oldest soil is but slightly different from that of the youngest, whereas the amount of exchangeable hydrogen has increased very greatly. From the over-all point of view, virtually all of the newly formed exchange capacity has been occupied by hydrogen.

Although the total exchangeable base function has changed but slightly in comparison to hydrogen, the trends in it may be significant. The upward shift in the 27–60-year period, so characteristic of many

properties in this sequence, is quite probably related to the large deposit of pine needles during that time. The subsequent long downward slope from 166 to 60 m.e. per profile may indicate the long-term replacement-leaching action by humic acids and by carbon-dioxide saturated percolating waters, modified, no doubt, by a more or less steady replenishment of bases from parent material minerals.

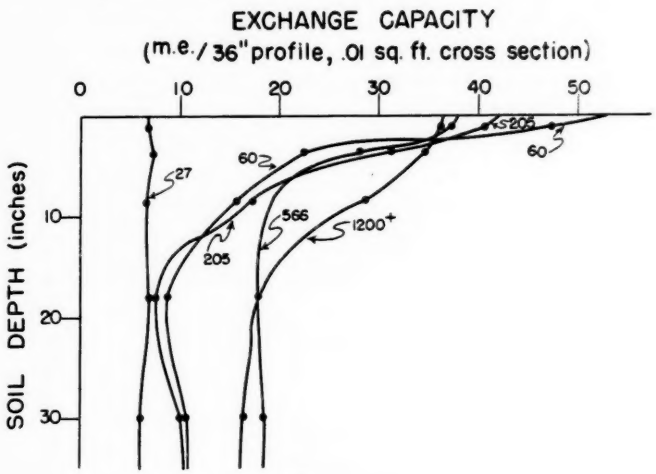

FIG. 9.

In Fig. 10 the quantities of exchangeable cations per profile have been converted to a percentage saturation basis. Although this results in a distortion of the volumetric picture, it is considered valuable in connexion with soil fertility problems. It is of special interest in this regard that the per cent. saturation of calcium fell well below what is considered to be critical nutritional values (Vlamis, 1949) in the two oldest members of the sequence.

The depth functions for per cent. base saturation (Fig. 11) provide some interesting information with respect to profile differentiation. The same curves also represent per cent. hydrogen saturation if the horizontal scale is reversed. During the first 60 years the per cent. hydrogen saturation increased, starting at the surface and gradually extending in depth. This trend continued in the next period up to the 205-year mark, except that the surface 2½ in. indicate the initiation of a reverse trend, in which the per cent. base saturation increased to a value 11 per cent. greater than that of the 60-year soil and perhaps 20 to 25 per cent. greater than the value expected from the earlier trend. The significant feature of the older depth functions was that, although the whole profile and the subsoil in particular continued the trend of increasing hydrogen saturation, the surface 2½ in. maintained the characteristic of a relatively higher base saturation than the layers below. It seems most likely that this profile differentiation is due largely to the cyclicly redeposited bases from the vegetation.

In Fig. 12 the corresponding depth functions for per cent. calcium saturation are given. Not only does the above discussion on total bases apply here, but also it is seen, by comparison of the figures, that most

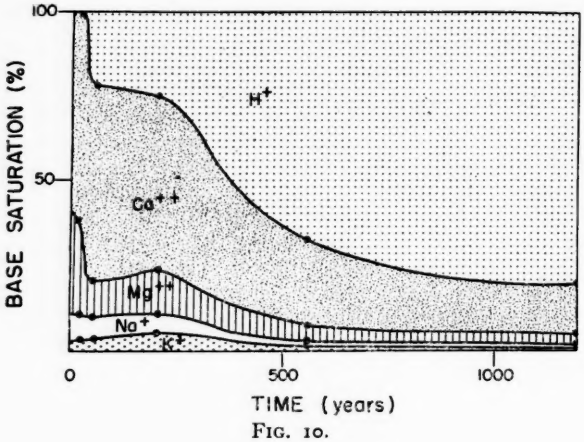

FIG. 10.

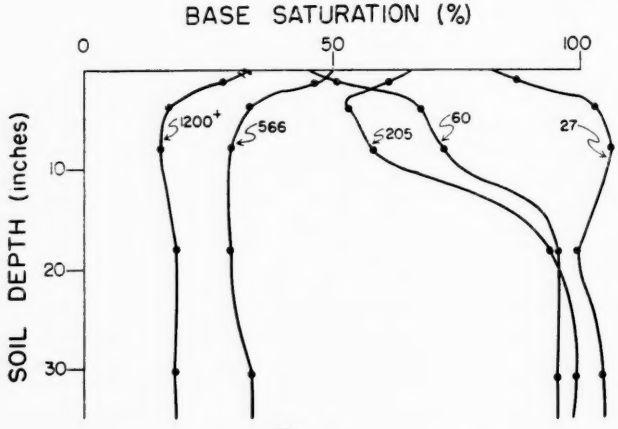

FIG. 11.

of the effect is due to calcium. If a corresponding plot for magnesium is made, similar trends are seen although they are of lesser magnitude.

The variations in the depth functions for sodium and potassium were small, ranging from 0 to 10 per cent., but nevertheless certain trends may be regarded as meaningful. In the case of potassium, the depth function at 27 years was comparatively uniform at about 4 per cent. At the 60-year mark the values had diminished at the surface and increased in the subsoil. At the 205-year stage a more exaggerated downward slope

prevailed at a higher level of potassium saturation, in which the subsoil attained a value of 9·5 per cent. and the surface returned to the value of about 4 per cent. In the years following this the potassium was diminished to nearly uniform values of 1·7 per cent. at 566 years and 0·5 per cent. at 1,200+ years. The sodium depth functions had similar characteristics.

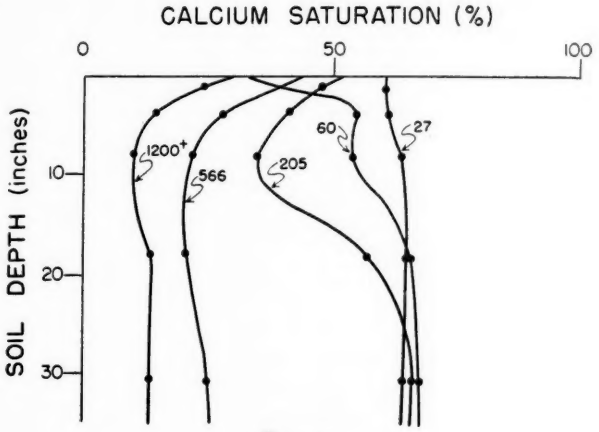

FIG. 12.

The principal differences between the K-Na and the Ca-Mg depth functions lie in the tendency of the former to show temporary relative accumulation in the subsoil of the younger members and lack of relative accumulation at the surface in the older members. These differences are probably best explained by the corresponding differences in cation properties, namely, ease of replacement and mobility, and probably also by the fact that the cyclic redeposition from the vegetation is quantitatively different for each of these elements.

Particle size analysis

The particle size analysis of the samples, as determined by the hydrometer method (Bouyoucos, 1936; Day, 1950), is given in Table 4, expressed as per cent. by weight of organic matter-free and gravel-free soil.

The most striking feature of this data is the general uniformity throughout. The weathering of rock and mineral particles appears to have been exceedingly slight, and it is perhaps doubtful whether certain slight trends are due to soil-formation processes or simply due to small variations in the original material. The higher clay values in the surface samples may be partly due to remnants of the organic matter which proved extremely difficult to destroy completely with hydrogen peroxide.

Mineralogical analysis

The fine sand fraction (0·25–0·1 mm.) of the soils was separated into heavy and light components by the use of bromoform (specific gravity

2·8). Ten of these samples representing the 27-year and 1,200+-year profiles were subjected to further mineralogical examination. In the heavy fractions the magnetite and magnetite-rich minerals were separated by means of a magnet. The heavy minerals, light minerals, and magnetite data are expressed as per cent. by weight. The mineralogy of the remaining heavy minerals and the light minerals was determined by direct count from a series of line transects of the mount and expressed as per cent. by number, based on 300 to 500 grains.

TABLE 4

Particle Size Analysis

Depth (in.)	*Soil age*	*Per cent. organic-free soil*							
		mm. 2–0·5	*mm. 0·5–0·25*	*mm. 0·25–0·1*	*mm. 0·1–0·05*	*μ 50–30·4*	*μ 30·4–3·8*	*μ 3·8–1·5*	*μ 1·5*
0–2½	27	34·1	15·8	23·8	14·7	1·2	6·6	0·6	3·2
	60	24·7	14·6	23·2	14·1	8·0	8·4	1·7	5·3
	205	35·7	15·1	22·1	12·1	0·9	6·7	1·2	6·2
	566	26·7	13·8	20·2	14·6	4·2	12·1	2·1	6·3
	1,200+	27·8	14·5	21·4	14·2	1·4	12·3	2·8	5·6
2½–5	27	28·1	15·6	25·3	13·6	5·8	7·9	1·9	1·8
	60	29·2	15·6	23·6	14·4	3·6	7·9	1·3	4·4
	205	30·7	16·5	26·1	13·0	2·0	6·7	1·2	3·8
	566	26·9	14·4	22·4	15·5	2·7	10·9	2·2	5·0
	1,200+	23·3	14·2	22·9	15·6	3·1	15·6	0·3	5·0
5–12	27	32·5	16·0	24·5	12·4	3·1	8·1	2·2	1·2
	60	30·0	15·5	23·7	13·0	3·6	8·8	1·5	3·9
	205	29·7	16·4	26·7	14·6	1·7	6·3	1·1	3·5
	566	29·3	15·3	22·4	15·6	2·9	8·7	1·4	4·4
	1,200+	25·7	14·1	23·1	15·7	2·4	11·9	2·5	4·6
12–24	27	31·0	15·7	24·8	12·3	5·2	7·4	2·0	1·6
	60	26·6	15·8	25·5	14·3	5·3	8·7	2·1	1·7
	205	34·5	17·3	23·8	11·7	6·1	4·0	1·5	1·1
	566	31·4	15·5	23·5	13·2	2·4	8·3	2·1	3·6
	1,200+	31·4	17·0	25·1	13·2	1·8	6·9	1·8	2·8
24–36	27	37·1	13·1	19·2	12·3	5·7	8·4	2·1	2·1
	60	25·0	15·3	24·5	14·8	6·8	8·8	3·1	1·7
	205	26·1	16·0	26·1	14·2	4·9	9·0	1·8	1·9
	566	29·5	16·2	25·7	13·7	1·8	7·6	1·8	3·7
	1,200+	27·8	16·8	25·3	14·2	3·5	8·4	2·3	1·7

The variations in heavy particle and magnetite contents of the fine sand fraction (Table 5) are considered to be due to minor variations in the parent materials rather than to the effects of soil-forming processes.

Both apatite and zircon occurred exceedingly rarely in the heavy fractions, but not a single grain was counted in the transects. A large proportion of the heavy minerals, especially the pyroxenes, had remnants of volcanic glass and occasionally volcanic rock adhering to them.

The light fractions were made up almost entirely of fragments of volcanic rock and basic plagioclase feldspar. The plagioclase was predominantly labradorite. The plagioclase crystals frequently had small pieces of volcanic rock adhering to them. The small amount of glass was

usually cloudy because of microlithic crystal inclusions. Some pieces of glass were dark or even black and, under reflected light, some pieces were rose-coloured or pale green.

The only evidence of weathering, which was at all obvious under the microscope, was confined to the volcanic glass. In the older soils this gave rise to an opaque appearance of most of the individual grains owing to the weathering of the glass incrustations.

TABLE 5

Heavy Particle Content of Fine Sands (% *by weight*)

	Total heavy fraction					*Magnetite fraction*	
Depth (in.)	*27 years*	*60 years*	*205 years*	*566 years*	*1,200+ years*	*27 years*	*1,200+ years*
0–2½	13·2	16·6	16·6	20·0	22·6	2·6	2·7
2½–5	18·2	17·4	16·0	18·8	22·4	2·6	2·6
5–12	19·8	17·4	14·0	18·8	23·4	2·5	2·7
12–24	18·8	21·4	21·8	22·4	23·0	2·6	2·5
24–36	17·6	18·4	18·8	21·6	22·4	1·8	1·8

A comparison of the data for the youngest and oldest profiles (Table 6) suggests that the amphiboles have decreased and the pyroxenes have increased with time, but since the same difference was found in the parent material samples (Dickson and Crocker, 1953*a*), it is not believed to be due to soil-formation processes. The random nature of the depth functions lend support to this view.

In general it may be concluded that the soil-formation processes have not yet affected the mineralogy of the fine sand fraction of the soils in any important manner except for the qualitative observation of glass weathering.

Samples of the organic-free, calcium-saturated clay fraction were subjected to differential thermal and X-ray analyses.* The results indicated clearly that there were small quantities of a montmorillonitic mineral in the parent material samples, accounting perhaps for their small but significant exchange capacities (approximately 2 m.e./100 g.). The analyses also showed that there was no kaolinite in any of the samples. Although the differential thermal curves showed an endothermic reaction in the 70° C. to 265° C. range which increased with soil age and decreased with soil depth, the X-ray patterns became increasingly diffuse and unidentifiable. This suggested that a mineralogical change may have taken place in the clay fraction, without increasing the amount of clay, but the precise nature of the change (if real) was not elucidated.

Discussion

Before commencing a discussion of the particular content of this paper it is perhaps desirable to review the relationship of the *selected profiles* to the ecosystem as a whole. It will be realized at once that the initial paper of this series was concerned with a much broader, natural, system

* The assistance of Dr. I. Barshad in this phase is gratefully acknowledged.

than that employed herein. The selected soil profiles represent only a few square feet of land surface, at the most, and the question naturally arises as to the degree to which the results may be considered to have areal extent. Other than the making of inspections in the field, the authors made no attempt to evaluate soil variability on the mudflows. It is our opinion that in the visual characteristics of the mineral soils, aside from their stone contents, and different individual plants from one

TABLE 6

Mineralogy of Magnetite-free Fine Sands (% *by number*)

Depth (in.)	*0–2½*	*2½–5*	*5–12*	*12–24*	*24–36*
	27-year profile, heavy fraction				
Hypersthene	62·6	63·7	60·0	66·8	65·3
Augite	3·0	2·3	2·5	2·6	3·0
Hornblende	21·2	23·0	28·5	19·7	21·3
Basaltic hornblende	13·2	11·0	9·0	10·9	10·3
	27-year profile, light fraction				
Plagioclase	36·5	36·8	41·8	45·2	40·0
Glass	4·9	6·7	4·0	2·8	7·3
Rock	58·6	56·5	54·2	52·0	52·6
	1,200+ -year profile, heavy fraction				
Hypersthene	82·9	85·3	85·5	78·2	83·0
Augite	5·7	3·3	6·3	7·6	6·3
Hornblende	6·3	6·7	4·7	8·5	7·0
Basaltic hornblende	5·1	4·7	3·5	5·7	3·7
	1,200+ -year profile, light fraction				
Plagioclase	30·6	32·2	35·7	36·7	34·8
Glass	13·2	14·8	8·6	9·7	12·1
Rock	56·3	53·0	55·7	53·7	53·1

point to another, the variability was small by comparison to the rather large differences between time states. The variability related to the pattern of plant colonization was reduced in our study by confining ourselves to a species (*Pinus ponderosa*) which was present throughout the whole sequence.

The soil profiles were selected so as to meet as closely as possible the specifications inherent in Jenny's definition of a chronosequence, with the refinement that biotype effectiveness in pedogenesis was recognized. The principal criteria of site selection centred upon the choice of the zone of maximum (omitting the bark accession region immediately about the trunk) forest-floor accumulation under pine-trees, but included many other factors such as the avoidance of excessively high stone content, steep slopes, depressions, and eroded areas. Obviously other criteria might have been employed, resulting in a slightly different chronosequence. The validity of our selection, as well as our practice of drawing curves through the single observed points, is no doubt open to some criticisms and objections, of which we are openly conscious. Nevertheless it is our opinion that an accounting of these objections, while modifying the details, would not affect the validity of any major conclusions.

The variability in the vegetation and forest-floor portions of the ecosystem were described in the preceding papers.

In order to visualize the nature of the soil development more clearly it is advisable to integrate some of the salient features of the previous papers with those reported here. The initial sources of differentiation, which changed the barren mudflows into the body referred to as 'soil', can be broadly classified into two groups. The first of these is the germination and survival of the first effective disseminules, thus establishing, immediately, an (upper) organic phase and a (lower) inorganic phase in the system. The second source of differentiation might be regarded as the weathering aspect, in which is included such things as the entry of rain-water at the surface and the temperature gradient, thus establishing, immediately, a physico-chemical variation from the surface downward. Included in the first of these sources of differentiation would be the addition of micro-organisms, the nitrogen-fixing organisms in particular, which probably arrived chiefly through the agency of atmospheric dusts. As soon as some litter was deposited on the surface of the mudflow an organic matter depth gradient was initiated. Simultaneously, similar depth gradients for pH, apparent density, colour, exchange capacity, and, possibly, mineralogical changes came into being. With increased carbohydrate energy supply, nitrogen fixation became accelerated.

The deposition of organic matter on the surface (forest floor) was not regular, there being a period of large additions beginning just before the 60-year mark and continuing for many years following. During this time the overstocked young forest was thinning itself out. The accumulation of organic matter in the soil, below the forest floor, followed a pattern which reflected this irregularity. An examination of the data given in this paper reveals that several other properties developed along lines which were rather similar to that of the organic matter. Among these were the apparent density, colour, moisture characteristics, and exchange capacity.

The very scanty evidence of any mineralogical change in the clay fraction is probably of more than usual interest, and emphasizes how slow the formation of secondary clay minerals must be, if it occurs at all, in such an environment.

Although the pH changes appeared to be conditioned by the appearance of an organic phase, the pH time functions bore no obvious relation to any of the time functions described in this study, including exchangeable bases and exchangeable hydrogen. This indicated that the pH was influenced by, or in equilibrium with, some phase or properties of the system for which the analyses did not account. It seems plausible to consider the possibility of the pH time functions being related to the changes in the *qualitative* nature of the organic matter and, possibly, the clay minerals. Conceivably this might have resulted in differences in the exchange constants of the exchange complex at various points in time and might have given rise to different equilibrium values of non-absorbed hydrogen in relation to adsorbed hydrogen, and hence differences in pH.

The shape of the exchange capacity time curves reflected some of the major changes in the vegetation and, more particularly, the development

of the organic profile. The principal trend in the development of the exchangeable base profile was a rapid approach towards a low base saturation. This trend is related no doubt to the very acid nature of the decomposing litter at the surface. A depth function of bases (chiefly calcium) was initiated which appeared to be conditioned by the cyclic redepositing of bases on the soil surface in the form of leaf litter. In view of the extremely low level of base saturation in the oldest soils, it is believed that the cyclic re-use of bases by the vegetation is a key factor in the maintenance of nutritional sufficiency in these later stages.

The apparent absence of clay formation over the period of the sequence (1,200+ years) strongly suggests that, under these conditions, the development of a marked texture profile, if it is to occur at all, would require some order of geological, rather than historical, time. Nearby soils, presumably much older, which are developed on glacial till of similar mineralogical character, show no pronounced textural profile.

In view of the negligible changes in the texture of the mineral phase, the large and rapid changes in apparent density must be ascribed to the accumulation of organic matter. The process of change may be viewed as a 'puffing up' of the soil, although the exact mechanism remains obscure. If the organic matter had simply moved downward, filling the spaces between sand grains, the apparent density obviously would have increased. Additional processes such as repeated wetting (swelling) and drying, microbial activity and root development must have been involved also. On the basis of the apparent densities and a mean real density of 2·3* g./c.c. for the volcanic rock particles, the calculated porosity changed from about 30 per cent. in the parent material to about 60 per cent. in the surface 2½ in. of the older soils. The pore space, thus calculated, includes that which is occupied by organic matter.

The fact that free iron oxide did not appear to accumulate until after the 205-year stage is puzzling. The process involved did not appear to be related to any of the changes observed in other properties. Robinson (1949) has stressed that a lowering of the base status results in a partial decomposition of the clay complex whereby sesquioxides, principally hydrated ferric oxide, are liberated. Deb (1950) found it necessary to postulate a microbial mechanism for the precipitation of iron.

Although much of our data suggest that a steady state condition has been approximated, no ready means was available for testing this idea. It may be, for example, that the soil properties have merely reached a temporary steady state, or that the rate of change has become much slower. It is indeed clearly apparent from the depth functions that the two older soils had not reached a steady state. Furthermore, if we were to take soil depth as defined by the horizon where certain soil properties approach those of the initial (parent material) state, then our 36-in. profile does not include the whole soil body for the two oldest soils. Although the concentration (percentage content) of a property such as nitrogen in a given horizon *may* be destined to remain almost constant with time, the profile *may* continue to extend downward. In any case,

* This figure is probably low, but is the mean density of several rock fragments in the subsoil as determined by the water-displacement techniques.

the uncertain history of our oldest soil would be sufficient to deter us from considering that in our sequence there was anything more than an apparent steady state.

It is hoped that the present series of papers may serve to illustrate the potentialities of approaching studies on soil genesis from the broad standpoint of the ecosystem, where that is possible, rather than the more restricted views which are ordinarily assumed. The existence of interrelationship, for example, between 'plant succession' and 'soil' development is clearly indicated. The long delay of about 250 years before the cedars and firs could become successfully established in the forest was quite possibly dependent, amongst other things, upon the development of certain of the soil characteristics. Conversely, the drastic thinning-out process in the 60-year forest appeared to be a purely competitive circumstance, but, as the data indicated, it had significant effects on the course of soil development. The rapid accumulation of nitrogen on the initially barren mudflows not only influenced the growth rate of the pine-trees, as suggested previously, but surely must have affected the characteristics of the succeeding vegetative assemblages as well. Several such general examples of interrelationship are readily suggested although the actual processes are probably extremely complex. The study emphasizes the potential usefulness of chronosequences, wherever they may be found, as a means of elucidating the soil-forming processes.

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(*Received 29 October 1953*)

SOIL CLASSIFICATION IN SASKATCHEWAN, CANADA

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STUDIES in soil morphology, soil genesis, soil geography, and soil classification form the core of modern soil science or pedology. Advances in one field are likely to assist studies being made in the others. Studies in soil classification, for example, benefit from the extension of soil surveys into hitherto unmapped regions and from researches into the processes of soil formation. As stated by Simonson (1949), schemes of soil classification reflect the state of knowledge of soil science at the time of their formulation.

The foregoing statements suggest that any existing scheme of soil classification needs to be modified as new knowledge becomes available. This viewpoint is well illustrated by the history of soil classification in Saskatchewan over the past 30 years. The present paper deals briefly with the development of soil classification in this province, followed by a discussion of present problems.

Development of Soil Classification in Saskatchewan

A discussion of soil classification in Saskatchewan is inseparable from a discussion of the soil survey. The University Department of Soils was established in 1920—about the time that a Royal Commission of Inquiry into Farming Conditions was recommending the inauguration of a soil survey of the province to be conducted from the University. The development of systems of soil classification was therefore influenced from the outset by practical considerations: the classification units had to be mappable and had to emphasize soil characteristics that could be used to interpret the survey in terms of soil productivity and land utilization. The classification was also influenced by the broad scale of mapping made necessary by the large area to be covered.

Due to the above conditions some of the concepts of classification adopted or developed in Saskatchewan may be said to exhibit a strong regional bias. This is a disadvantage from the standpoint of fitting the classification into a world system. On the other hand, there are also advantages in having to apply a classification system to soil mapping and to the rating of agricultural lands; for one thing, it eliminates the possibility of devising a system that cannot be used in the field to separate soil areas, and thus ensures that the soil is recognized as a geographical body. Some otherwise worthy schemes of classification, such as those based upon chemical properties, have the inherent weakness that they cannot be used by the soil surveyor.

The development of soil classification in Saskatchewan is recorded in the thirteen major soil-survey reports published between 1923 and 1950. The reports indicate the changes from the early classifications based largely upon soil textures to the present system based upon the morphology, composition, genesis, and site characteristics of the soil profile.

Journal of Soil Science, Vol. 5, No. 2, 1954.

The classification used in the first soil surveys was based upon the systems used by American workers. Roy Hansen, first Professor of Soils at Saskatchewan, was influenced by the system then in use in the State of Illinois; this included the textural class as the main mapping unit, the observation of soil colours, the listing of soils by means of assigned numbers, and the sampling of soils at arbitrary depths.

The first advances in soil classification came partly from the contributions of pedologists in other regions and partly from the knowledge gained through soil-survey work in Saskatchewan. This dual influence is indicated in a paper by Joel (1926), who succeeded Hansen as head of the Department of Soils. In this paper Joel made reference to Marbut, to the American Soil Survey Association, and to the International Society of Soil Science, as sources of information on a new approach to soil classification; he also emphasized the need for an effective system of soil classification comparable to those established in other physical sciences; in addition, he discussed certain Saskatchewan soils from the new viewpoint of using the natural soil profile as the basic unit in classification. This was the first paper from western Canada to deal with the more modern concepts of pedology.

Subsequent papers by Joel (1927, 1928, 1932, 1933) indicate further changes in the classification as the study of Saskatchewan soils proceeded. As before, these changes were influenced by access to the publications of pedologists from other regions, the introduction of the Russian viewpoint being particularly important (Glinka, 1927; Afanasiev, 1927; Zakharov, 1927; Marbut, 1928). Soil classification was also influenced during this period by direct contact between Saskatchewan workers and those in adjoining provinces and by visitors from other regions. Marbut visited western Canada in 1925, and in 1927 members of the International Congress of Soil Science toured the region.

The changes in the classification of Saskatchewan soils referred to above included greater emphasis on soil-forming factors, soil genesis, and soil morphology, together with a growing realization of the complexity of the geographical distribution of soils. The work of Joel as a teacher and as director of the soil survey from 1924 to 1933 laid the foundations for the developments in soil classification and soil survey which have occurred since that time. His field studies on the site characteristics and morphology of Saskatchewan soil profiles deserve special mention.

During this same period, F. H. Edmunds conducted the first Saskatchewan studies on geology in relation to the soil survey (1929); he also contributed to an understanding of the physiography of southern Saskatchewan. Since 1926 he has been largely responsible for the section of each soil-survey report dealing with geology in relation to soils.

From 1929 to 1932 the Dominion Department of Agriculture cooperated in soil-survey work by providing funds for additional staff and equipment. The enlargement of the staff made it possible for the Saskatchewan Soil Survey to proceed with a broad reconnaissance survey of the settled portion of the province. This broader type of survey was made necessary by the increasing demands for soil information, which

could not be met quickly enough by the more detailed surveys. As the work progressed it became increasingly apparent that the classification based upon soil series and type as defined by the United States Bureau of Soils was inadequate for the survey; the scale of mapping was too broad to permit the separation of true series types even in the more uniform areas; in many instances the local soils formed such a complex pattern that several potential series might be encountered within a radius of a few yards.

The co-operative work in soil survey came to a temporary halt in 1932 due to the economic depression. The work was not fully resumed until 1936, when the Saskatchewan Soil Survey, under the direction of Professor J. Mitchell, carried out special surveys in the drought-stricken areas (Moss, 1937). In addition, the broad reconnaissance survey was extended into the partially settled forest areas of the north. The problem of finding a more suitable system of soil classification was also investigated.

The revised Saskatchewan classification was finally completed in 1940. It was based upon the work of Ellis, who had established a system of classification for the Manitoba Soil Survey. This system, in turn, was based upon a scheme developed by Nikiforoff. As presented by Ellis (1932) the system provides that genetic soil profiles, found together on the same geological parent material in any given physiographic region, are grouped together to form a soil association. The individual soil profiles, known as associates, are separated on the basis of morphological differences which are largely the result of topographic conditions responsible for changes in the soil climate. As Ellis pointed out, the system shows the relationship of soils found in association in the field and also simplifies soil mapping.

The concept of the soil association has greatly influenced soil classification and soil mapping in Canada. In 1945 it was adopted by the National Soil Survey Committee (1945), a body representing all soil-survey organizations in Canada. It has also been adopted by the Scottish Soil Survey (Glentworth and Dion, 1949). In view of this development it is unfortunate that the Manitoba work did not attract more attention outside Canada. For one thing, the word 'association' now has two meanings—a group of related soils as in Canada, and a cartographical unit composed of several or many series, not necessarily related, as in the U.S.A. Furthermore, the Canadian association is now identical with the present concept of Milne's catena. It is somewhat surprising, therefore, that more recent papers (Bushnell, 1945; Winters, 1949) dealing with the origin and use of the catena concept should contain no reference to the Canadian soil association.

Present Classification of Saskatchewan Soils

An outline of the present classification is given in Table 1. In all significant features it is similar to the classification adopted by the National Soil Survey Committee (1945). The definitions of the various units reflect the viewpoints of Saskatchewan workers. The system is designed to provide units or categories that can be used in classifying and mapping Saskatchewan soils.

The concepts of regional and zonal soils are easily applied in the field to the separation and mapping of soil regions and soil zones respectively. The soil association forms the major mapping unit of the reconnaissance soil survey. In such surveys the broad scale of mapping and the complexity of most soil areas make it impossible to use the member (series) profile as the basic mapping unit. However, the various member profiles must be identified before the association can be fully described. In this way the member profile constitutes an important unit in the classification

TABLE 1

Key to Classification of Saskatchewan Soils

1. Regional Soil Profiles.	Soils separated on differences in profile features resulting from the effects of broad regional differences in climate and native vegetation: Grassland Soils; Forest Soils.
2. Zonal Profiles.	Soils separated chiefly on differences in the colours of the A horizons due to the effects of differences in climate and native vegetation occurring within a soil region. The differences in colour are associated with differences in organic-matter content of the A horizons. Differences in other morphological features may also help to identify different zonal soils, provided these soils are essentially similar in topography and parent material.
3. Soil-Association (Catena) Profiles.	A group of related soils belonging to the same zone and developed on similar parent materials. Within each zone a soil association is established for soils occurring on each separate kind of parent material.
4. Soil-Member (Associate or Series) Profiles.	The individual soils forming an association, separated from each other by profile differences due to differences in topographic features (slope, aspect, micro-relief), drainage, and stage of maturity.
5. Soil Textural Classes.	Any soil unit separated on the basis of the dominant texture or textures (mechanical composition) of the surface horizons and, if required, of lower horizons as well.
6. Topographic Classes.	Any soil unit separated on the basis of variations in surface features (degree, shape and frequency of slopes) that are significant to the recognition of soil landscapes. In most instances the topographic units will also be significant to land use.
7. Stony Classes.	Any soil unit separated on the basis of degrees of stoniness that are significant to land use.

although it may not form a mappable unit in all surveys. The textural, topographic, and stony classes may be applied to any classification unit that can be separated in the field and shown on the soil map. For example, a given soil association may be subdivided on the map according to differences in the dominant texture, topographic features, or degrees of stoniness occurring in the field.

Considering the classification in more detail, the concept of regional soils is intended to provide a primary grouping of the soils of Canada. Major regional groups so far established are grassland, forest, and tundra soils. It may be necessary to establish other regional groups or subgroups; it is possible, for example, that the far northern section of Saskatchewan may contain a transition belt of forest-tundra soils (Halliday, 1937). At present, however, only the grassland soils and the southern

portion of the forest soils have been studied in this province. In a broad way, the grassland soils represent kinds of soil formation which result in the accumulation of humus in the mineral A horizons of the profiles, whereas the forest soils are characterized by accumulations of organic materials (A_0 and peat horizons) above the mineral soil.

The zonal soils represent subdivisions of the regional soils, and in most instances are used as the first unit or category in classifying or mapping the soils of a given area. The first soil map of Saskatchewan (unpublished) was a map of the major soil zones. The zonal soils of the grassland region—brown, dark brown, and black—represent Saskatchewan varieties of world soils known generally as brown, chestnut, and chernozem soils. The black-grey soils represent transitional types between chernozemic and podzolic soils (degraded black soils). The grey soils represent podzolic types.

In identifying regional and zonal soils, or in mapping soil zones, chief consideration is given to profile features reflecting the influence of the climatic and biologic factors of soil formation.

The parent-material factor is introduced with the soil association; an association is defined by the kinds of profiles occurring on a given type of parent material, as: Haverhill Association—brown, medium-textured soils, chiefly columnar (prismatic) and solonetzic profiles, developed on calcareous boulder clay. In the ordinary reconnaissance survey the columnar, solonetzic, and other member profiles are not separated on the soil map. The association described above is indicated on the map by symbols representing the association name, the dominant texture, and the topographic class. However, the various member profiles are described in the soil-survey report, together with a statement on the relative catenary position or topographic site occupied by each. Thus it is possible to provide considerable information to assist in the interpretation of local soil conditions occurring within an area mapped as a given soil association.

The classification scheme outlined in Table 1 has proved satisfactory for its main purposes—the identification and mapping of Saskatchewan soils with particular reference to reconnaissance soil surveys. However, a number of problems remain to be solved. These relate both to the future use of the classification in Saskatchewan and to the position of Saskatchewan soils in a world-wide scheme of classification.

Classification Problems

(*a*) *Saskatchewan problems*

With respect to future work in Saskatchewan the classification system must be suitable for carrying out and interpreting detailed soil surveys. In some instances it is possible to separate areas consisting chiefly of profiles belonging to one association member. This member corresponds to the prevailing concept of the soil series, and if textural classes are separated a unit corresponding to the series type may be established and mapped. Where this is possible one might conclude that the soil series should be regarded as the basic unit of the classification.

There are two objections to this viewpoint. In the first place the

potential soil series discussed above is still a member of an established association or catena. By classifying and naming this member as a separate soil series, its relationship to other member profiles of the association is no longer apparent. The second objection is more of a regional problem. In many parts of southern Saskatchewan a number of potential series may occur in close association, forming local soil patterns of extreme complexity. It is not possible to separate every potential member or series profile on any practicable scale of mapping. This condition is associated with a complex micro-relief due to glaciation, together with the influence of a semi-arid to sub-humid continental climate. The result is that soil-moisture efficiency varies greatly with variations in slope, aspect, drainage, vegetation, and texture. The variations in soil climate result in the development of different soil profiles within a small local area. Many of these complex soil areas are covered in special soil surveys carried out between 1939 and 1949 (Clayton and Ellis, 1952).

A field study of the local complexity of Saskatchewan soils was made by Treleaven (1949) followed by laboratory studies of the same soils by Rennie (1949). Some of the data collected by these authors are presented below.

The area selected for study was a portion of a very gently rolling glacial plain lying just within the black-soil zone. The actual site was a 'wavy' or undulating slope with a northerly aspect. The slope extended from a low knoll down to a shallow depression, a horizontal distance of 72 ft. The difference in elevation between the crest of the knoll and the depression amounted to 4 ft. 8 in. Within this short slope five soil profiles were selected for study—I, black thin (truncated) knoll; II, black solonetz-like; III, slightly degraded black; IV, degraded black; and V, depression grey podzolic ('bluff' podzol). The last-named soil was developed on local alluvial or pond deposits overlying the calcareous boulder clay which formed the parent material of the other profiles. The native vegetation included grasses, shrubs, and trees (aspen), forming the following sequence: grasses on the black soils—profiles I and II; shrubs and some grass on the slightly degraded black soils—profile III; and aspen and shrubs on the degraded and depression podzolic soils—profiles IV and V.

The chemical data on pH values, soluble salts, inorganic carbon, and nitrogen correlate well with the morphological differences expressed by the above profiles. pH values of the A horizons ranged from about pH 8·0 in the truncated knoll profile to pH 5·1 in the A_2 of the depressional podzolic profile. Slight concentrations of soluble salts were present in the C_1 horizon of the knoll profile, 1·3 per cent. in the C horizon of the solonetz-like profile, and none in the remaining profiles. Inorganic carbon, reported as lime carbonate, was present in the A horizon of the knoll profile; in the solonetz-like and the degraded black soils the highest concentration of $CaCO_3$ occurred in B (ca) horizons, while in the depression podzolic profile only slight amounts remained in the lowest B horizon. The parent materials of all soils were very calcareous, containing 17–20 per cent. lime carbonate, reported as $CaCO_3$.

The organic-matter content (determined by N × 20) of the A_1 horizons of the thin knoll, solonetz-like, and slightly degraded profiles ranged from 6 to 7·5 per cent.; the A_1 of the degraded black profile contained 3·3 per cent. organic matter, and the A_1 of the depression podzolic contained 6 per cent.—this, however, representing a very thin horizon (1·5 in.). In the degraded black and depression podzolic profiles the A_2 horizons contained less organic matter than the B_1 horizons, an indication of podzolic leaching.

It will be evident that each of the profiles studied by Treleaven (1949) and Rennie (1949) represents a potential soil series, with the possible exception that the two degraded profiles might be placed in the same series. It is equally evident that these series cannot be mapped separately in reconnaissance or ordinary detailed mapping. It would appear that in the most detailed survey that could be regarded as practicable, not more than three, and possibly only two, map units could be established. Profiles I and II, representing grassland black soils, might be separated from profiles III to V, representing wooded degraded (podzolic) soils. If the depression were large enough to map, the depression podzolic soil would be separated from the degraded black types since the former soil is developed on different parent material.

In addition to the excessive cost of mapping a whole region in very great detail, the type of agriculture prevailing in Saskatchewan does not warrant the separation of all potential series types. The farms are large (averaging about the 500 acres) and grain, chiefly wheat, is the dominant crop. In the soil complex discussed above, all of the soils are arable. The depression podzolic soil may be too wet in the springtime to permit sowing with the rest of the soil areas, but it may be sown later, possibly to oats if the season is late. The important point is that, with the above possible exception, the various soils will be cultivated and cropped as a single unit. Hence while it is essential that the soil surveyor should know what soils are present, it may not be necessary from the practical point of view to attempt to map all of them. Instead the surveyor endeavours to map the most significant soil combinations and uses the soil-survey report to describe the individual types in detail.

Where a combination of complex and relatively uniform soil areas occurs, a detailed soil map might show soil associations or catenas, segments of catenas, and single catenary members or series. It is obvious that such a situation poses serious problems in establishing a logical classification and map legend and in recommending systems of land use and soil management. In the soil area studied by Treleaven (1949) and Rennie (1949) the classification problem is complicated by the fact that both black (chernozemic) and degraded black (podzolic) soils are present. By the definition of the soil association adopted in Saskatchewan, these soils represent a complex of soil associations—the black soils, profiles I and II, belonging to the Oxbow Association and the degraded black, profiles II and IV, belonging to the Whitewood Association. According to prevailing definitions all of these soils belong to a single catena.

There are two reasons for regarding the above complex of black and degraded black soils as a complex of two associations. In the first place,

by restricting the soil association to soils formed on similar parent materials and belonging to the same zone, the association becomes a classification unit as well as a mapping unit. Secondly, areas of the black (Oxbow) soils occur in which no Whitewood soils are present; conversely, areas of Whitewood soils occur as an association or catena of degraded black soils, with no black types present. In short, the Oxbow and Whitewood soils represent two separate associations or catenas. Where both Oxbow and Whitewood soils occur in close association they must either be classified as a new soil association or treated as a complex of existing associations. The latter appears to be the more logical decision.

It would seem therefore that in Saskatchewan the soil association should be retained as the major classification unit to be shown on the soil map. Wherever possible the dominant member (series) profile or combinations of two or more important members should be separated and indicated by appropriate symbols following the association symbol. The various member profiles will thus be linked by their common parent material and zonal characteristics, as implied by the association name. Otherwise, if individual member profiles are classified as separate series, the main result would be a multiplicity of unrelated series names.

The foregoing discussion may be open to criticism on the grounds that it deals with problems of soil mapping rather than soil classification. However, it has already been pointed out that the Saskatchewan soil classification is used mainly to identify and map soils in connexion with the soil-survey work. Furthermore, it is not suggested that the methods and viewpoints expressed herein are necessarily applicable or valid in other parts of the world. The discussion has attempted to outline the particular classification problems associated with Saskatchewan conditions, and thus to indicate the reasons for establishing the present classification.

(*b*) *World problems*

No attempt will be made here to discuss world problems in soil classification except as they affect the position of Saskatchewan soils. According to the viewpoint shared by Saskatchewan workers more knowledge of world soils is required before a comprehensive and satisfactory world system of classification can be established. It is also considered that universally acceptable definitions of major world soils and genetic processes should be agreed upon before attempting to create a system of classification for the soils of the world.

Applying these statements to Saskatchewan it is believed that the first problem is to describe and define Saskatchewan soils as fully and as clearly as possible. In this way workers in other regions may secure a clear picture of the characteristics of Saskatchewan soils and so be able to compare them with types found in other parts of the world.

The most useful studies can be made on representative genetic profiles. These profiles, when identified on a particular parent material within a particular soil zone, become the member profiles of a given soil association. From the standpoint of a world-wide classification it is desirable to consider these soils as genetic types before they are placed in various

associations. This can be accomplished by establishing a category of 'Principal Genetic Profiles' above the association and, if desired, above the zonal soils also. The principal genetic profiles so far recognized in Saskatchewan are listed in Table 2. Space does not permit a description of each type of profile, but brief descriptions of most of the soils have been given by Mitchell, Moss, and Clayton (1947, 1950) and Mitchell and Moss (1948).

TABLE 2

Principal Genetic Profiles in Saskatchewan

Weakly developed soils	No to slight profile development
Brown dark brown or black soils of grassland	granular calcareous (high lime)
	columnar calcareous (calcareous earth)
	cloddy-granular (clay)
	massive (compact clay)
	columnar (prismatic)
	saline (solonchak)
	alkali solonetz
	solonetz
	solodized-solonetz
	solod
	depression solodic.
Black grey-soils of grassland-forest transition	wooded calcareous (rendzina-like)
	wooded columnar calcareous (wooded calcareous earth)
	wooded leached calcareous (degraded rendzina-like)
	slightly degraded black
	degraded black
	degraded black-solonetzic
Grey (podzolic) soils of forest	brownish-grey podzolic (grey wooded)
	grey podzolic (grey wooded)
	grey podzolic-solonetzic
	grey podzolic sand
	depression grey podzolic
	podzol
Meadow soils of grassland and forest	meadow (wiesenboden)
	leached meadow
Organic soils of forest and grassland	organic mineral: gley-like (half-bog)
	organic mineral: humic
	organic mineral: degraded
	organic mineral: podzolic
	organic mineral: solonetzic
	organic: sedge peat (peat or bog)
	organic: moss peat (peat or bog)

The list covers the soils so far investigated in Saskatchewan. It is probable that other genetic profiles remain to be recognized or discovered. Among these may be the regrading solod, in which a solod profile completely leached of lime carbonate and salts is developing a secondary B horizon within the former leached horizons. Soils answering to this description have been observed, but it is not known what genetic process is replacing the solodic leaching. Another profile that may occur is that of the gley soil. So far Saskatchewan workers have not gone

beyond describing individual soil horizons as 'gley-like'. It has been hoped that a clearer definition of gley soils and gley formation will be forthcoming, particularly since there appear to be discrepancies in the use of these terms by various workers. Other profiles not yet studied are those associated with perpetually frozen soils, which are known to occur in far northern Saskatchewan.

The genetic soil profiles listed in Table 2 are identified chiefly by morphological features that can be recognized in field studies. To the extent that knowledge is available or theories of soil genesis appear applicable, genetic processes of soil formation are identified with the various profiles. To a limited extent laboratory studies have been made to assist in characterizing the profiles and defining the genetic processes, and this work is being expanded. It will be apparent that most of the principal profiles listed are Saskatchewan varieties of established great-soil-group profiles. Some profiles, notably the degraded black-solonetzic, the podzolic-solonetzic, depression grey podzolic, cloddy-granular, wooded columnar calcareous, and brownish-grey podzolic, are not easily identified with recognized world groups. There are other profiles whose definitions in Saskatchewan may not agree with the generally accepted definitions. Such profiles include the solonetz, which in Saskatchewan may be a soil with the morphology of the solonetz, but which lacks the chemical characteristics originally ascribed to this soil. Because of these differences the Saskatchewan soils are listed as principal genetic profiles rather than as great soil groups.

If more knowledge of the principal genetic profiles and their genesis can be acquired, it should be possible to place all Saskatchewan soils in their respective world groups. In the opinion of Saskatchewan workers it is unnecessary to devise a world classification which covers all categories down to local mapping units. Soil scientists in other regions do not require detailed descriptions of soil associations or soil series as such. What they do need are good descriptions and related laboratory data for all genetic profiles, and some idea of the geographical distribution of the dominant soils of each region. With this information it should be possible to establish a sufficient number of higher categories to permit a logical and not too cumbersome grouping of the soils of the world.

As already indicated, this objective, in the opinion of the author, cannot be attained until satisfactory definitions of genetic profiles and genetic processes have been agreed upon. At the present time it is suggested that advances in world classification are also handicapped by other factors, as indicated below.

1. *The lack of universally accepted definitions.* This point has already been mentioned, but it also includes questions of nomenclature. Robinson (1950) and Wilde (1953) have discussed the problem. The author does not agree with Wilde that we should turn to simple folk terms to describe world soils. There are already too many terms which began as comparatively local terms. One of Wilde's suggestions is the use of the term 'muskeg'. Local use of this word is by no means uniform even in Saskatchewan, and its adoption throughout North America as a soil name would be useless—unless it was strictly defined. Soil scientists

should certainly seek to secure better names for world soils, but the definition of the name in terms of soil characteristics and genesis is even more important.

2. *The tendency to dwell upon soil differences with the consequent neglect of soil similarities.* An outstanding example of this situation is the treatment of podzol and podzolic soils. These soils collectively have certain important characteristics in common—notably a relatively high soil-moisture efficiency which favours downward movement of soil water, conditions favouring the accumulation of 'raw' organic matter on or near the surface, the development of lighter coloured mineral horizons of eluviation and relatively dark coloured horizons of illuviation, and the removal in part or in whole of soluble salts, bases, iron, alumina, organic matter, and clay from the surface and the accumulation of some of these substances in the subsoils.

Despite these broad similarities no clearly defined category or unit of classification which will include all these soils has been agreed upon. Instead, strenuous efforts are made to show how brown podzolic soils differ from podzols, and how grey-brown podzolic, grey wooded and red-yellow podzolic soils differ from the first two and from each other. It is not implied here that these soils should not be separated—but only that they should be separated at lower levels than at present or, alternatively, that a new higher category is needed in which soils of all degrees of podzolic development can be defined. Whether the word 'podzol' or 'podzolic' should be retained is a minor matter, but probably a new term would be preferable for a new definition. It is unfortunate that the word 'podzolic' has not been accepted as a simple adjective, denoting all soils showing the effects of podzolization, irrespective of the degree to which this process has developed.

3. *The persistence of attempts to treat soils as biological rather than geographical bodies.* Robinson (1949) refers to the difficulty of applying a system of orders, genera, and species to the classification of soils. The acceptance of the soil as a geographical body would tend to simplify the establishment of the higher categories in a world classification. The use of terms such as tundra, forest, steppe, desert, &c., to denote regional soils has been criticized because these terms refer to climatic-vegetational regions rather than soils. This, however, is merely another example of the need for changes in nomenclature and for more precise definitions. The fact remains that every soil owes its characteristics to the combined effects of all the soil-forming factors, and that a given combination of these effects operates only at a certain location on the earth. No soil, as a complete natural body, can be brought into a laboratory or mounted on a wall. This fact is apt to be overlooked in studying monoliths or reading detailed descriptions of individual profiles. While the ten features proposed by Marbut (1922) for characterizing soil profiles are still the best criteria (Cline, 1950), it might be useful to add another factor—that of profile site. This should include the actual geographical location, elevation, land form, slope, aspect, vegetation, or land use. With this information at the head of every profile description, analysis, or monolith, the geographical nature of the soil would be less often overlooked.

The geographical viewpoint is supported in recent American work (Ableiter, 1949; Soil Survey Staff, 1951).

4. *The insistence by many pedologists that a classification system must be 'philosophical' or 'scientific' as opposed to the so-called practical schemes.* As an example, the use of the soil association (catena) has been criticized on the grounds that it does not represent a true scientific classification of soils. This is equivalent to saying that the grouping of native plants into an ecological association is less scientific than the botanical identification of each plant species. The fact is that the ecologist must be a botanist before he can be an ecologist; similarly the soil surveyor concerned with mapping a soil catena must be a pedologist before he is a soil surveyor—or more properly he must be a pedologist and a soil surveyor at the same time. The ecological associations and the soil associations are merely less precisely defined than their individual member plants and soil profiles respectively.

It is granted that some systems of soil classification are more scientific than others, but the more scientific the classification the more precise must be the facts on which it is based and the more sharply defined the objects which are classified. Present limitations in the knowledge of many world soils, and the fact that it is extremely difficult to define soil itself, suggest that soil science has not yet advanced to the stage where a complete and satisfactory world classification is possible. It should also be remembered that there are many ways of classifying natural objects and that each is suitable for its time and place if it fulfils the purpose for which it was designed.

Acknowledgement

The writer desires to thank Professor J. Mitchell (University of Saskatchewan) for helpful suggestions and criticism concerning the foregoing paper.

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(*Received 6 June 1953*)

WEATHERING OF MINERALS AS INDICATED BY PLANTS

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Introduction

THE minerals of the soil may under many circumstances play an important role as a direct source of nutrients for the plants. The term 'mineral', as used here, includes the primary minerals of the coarser fraction of the soil and some secondary minerals as well as clay minerals at different stages of weathering. In short, the term 'mineral' includes every variety of crystal in soil.

By weathering of minerals, either found in or added to the soil, important nutritional elements may be released and made more easily available to the plants. After weathering the released nutritional elements enter a cycle of changes between soil and soil solution through higher plants and micro-organisms and back through solution to the soil.

In various climates in the tropics and in temperate climates the minerals of the soil are often valuable as a source of nutrients for the plants. In temperate and humid climates the increases in yield, obtained by addition of different important plant nutrients, may be much larger on podzolized sandy soils than on loams or loamy soils. Furthermore, the visual symptoms of nutritional disorders are more generally observed on podzolized sandy soils than on loams and loamy soils richer in minerals. On the other hand, the minerals generally weather too slowly, even on loams, fully to supply the crop, and Novak (1938), who reviewed this subject in 1938, calls the primary minerals 'the iron rations of the crop'. This, of course, does not mean that the release of plant nutrients from such minerals by weathering may not be of some importance in temperate climates, with low temperatures most of the year and low rainfall as compared with the conditions found in the tropics.

In equatorial climates primary minerals have long been regarded as an important and ready supply of plant nutrients. Vageler (1933) is of the opinion that under equal conditions of trading and transport tropical soils are worthless unless their content of primary mineral is considerable. A large or medium content of such minerals is only found when the parent rock is rich and the soil is young. Van der Marel (1947), who worked with Indonesian soils, showed that the colloidal weathered fraction was nearly useless as a source of plant nutrients. For instance nearly the whole consumption by crops of potassium, calcium, and magnesium was released from the primary minerals andesine (potassium), bytownite (calcium), and hypersthene (magnesium). To quote van der Marel: 'It is clear then that under tropical conditions certain minerals can be important sources of nutrients to the plants. Not only the minerals that occur in a special type of soil but also the stage of weathering of the soil must be considered, for if a soil is so thoroughly

weathered that all readily decomposing minerals have been eliminated from it, it matters little to the plant what the origin of the soil may be. Furthermore, if the rocks in question have only a small inherent content of nutrients, deficiency symptoms will appear in the crops at a less advanced stage of weathering.'

Weathering of Minerals

In the laboratory many workers have studied the stages of weathering and the rate at which useful elements are released from different minerals by weathering. Such work has been done by chemical methods and in recent years by improved physical methods. But rather few have used the growth of the plant as an indicator of the release of nutrient elements during weathering either from individual minerals or from the coarser fractions, such as the sand or silt fractions, which may be isolated from various soil horizons, e.g. Graham (1941), Steenbjerg (1943*a*, *b*, 1951), Jones and Leeper (1951), Lewis and Eisenmenger (1948).

The use of plants as indicators is important for the measurement of weathering, partly because of the fertilizing value of, and partly because some plants are very sensitive to, some of the weathering products—ordinarily nutritional elements—when the experiments are performed under the right conditions. In fact it is often found that chemical and physical methods may be able to give some measure of the progress of weathering and indicate the final product of weathering; but such results may have no relation to the growth of plants. Van der Marel, for example, found that the mineral andesine is slightly soluble (weathers slowly) even when treated with concentrated hydrochloric acid, but when found in large amounts as in some Indonesian soils, it is able to supply most crops with the necessary potassium. Also opposite cases are well known. The phosphorus of apatite-bearing minerals is soluble in dilute acids, such as hydrochloric acid and nitric acid, but the crops are unable to utilize the phosphorus from these minerals in temperate climates; the supply is too small.

The weathering or decomposition of minerals as indicated by plants depends on several factors and some of their more important interactions, which alter the shape and the position of the yield curve, Steenbjerg (1952). These factors may be divided into four large groups.

1. *The soil factors in the widest sense*: pH value; humus (quantity and quality); the various minerals in the soil; amounts of available nitrogen, potassium, phosphorus, manganese, zinc, boron, copper, &c.; available water; surplus water; application of manure containing large amounts of organic matter, &c.
2. *Climatic factors*: temperature; humidity; light.
3. *The plant*: family; genus; species; variety.
4. *The stage of development of the harvested plant* (*time factor*).

Thus several factors influence the response plants give to the weathering of minerals. If, for instance, an experiment is performed with a mineral containing the plant nutrient potassium, and if the soil contains large amounts of exchangeable potassium; if further the amount of available

water is medium or low and the crop used does not need much potassium, the results may indicate a rather slow weathering, if any, of the potassium-bearing mineral in question, and especially so if the growing period is short (time factor). The same answer could be found if the soil used had a great power to fix the released potassium in new compounds very stable with respect to weathering and release of potassium.

This means that methods for measuring weathering by plants may be standardized either as done by Graham (1941), who used a hydrogen clay prepared from the heavy subsoil of the Putnam silt loam as the weathering agent, or the standardization may be fixed with respect to the more important soil conditions of larger or smaller areas, their climatic conditions, and the crops used in the areas in question. A highly standardized procedure as used by Graham may necessitate a very time-consuming evaluation of the experimental results as known from the verification of chemical soil and plant analyses (Steenbjerg, 1952). Besides, a highly standardized procedure may be dangerous because it seems reasonable to assume that the above-mentioned groups of factors, besides influencing plant growth and weathering, also influence the composition and nature of the new compound or compounds formed when the mineral tried in the experiment undergoes weathering.

Determination of Weathering

Method

In determining the weathering or decomposition of a slightly soluble mineral by means of plants the surface area and the nature of the mineral (the crystal lattice and the condition of the surface) are among the determinative factors.

The weathering rate (weathering per time unit) is of decisive and primary importance for the fertilizing value apart from all the primary effects and the interactions produced by the four groups of factors mentioned above, differing from one case to another.

To sum up: the weathering rate depends on several factors (several of which also influence plant growth), among which are the crystal lattice and the surface of the minerals. In the work of Jackson's *et al.* (1948) the weathering rate (weathering per time unit (t) is viewed as a product of an intensity and a capacity factor as outlined below.

$$\begin{aligned}\text{Weathering rate} &= \text{Intensity factor} \times \text{capacity factor} \\ &= f(\text{temperature, water, protons, electrons}) \\ &\quad \times (\text{surface, nature of mineral}).\end{aligned}$$

The weathering stage at any given time may then be represented schematically as a summation:

$$\text{Weathering stage} = \sum f(\text{Temp.}, H_2O, H^+, \Delta e^-, s, k_m, t).$$

The intensity factors of weathering are temperature (Temp.) with its relationship to humus formation, leaching by drainage (water), the acidity of the soil solution (proton intensity, H^+); furthermore, the degree of oxidation (electron intensity) and its fluctuation (oxidation-reduction, Δe^-). The capacity factors of weathering are the specific

surface of the particles (s) and the nature of the mineral (k_m) being weathered.

The weathering rates or the fertilizing values of minerals may be compared at different stages of weathering in various soils and climates; furthermore, one may be interested in comparing the weathering rates of two or several minerals containing the same nutritional elements, &c.

In such comparisons it seems important that the experimental results expressed in units of plant growth can be compared on the basis of the numbers of nutrient atoms on the very surfaces of the minerals in question. To explain further: if the numbers of nutrient atoms on the surfaces of the minerals can be calculated it is possible to compare the yield, found after addition (per unit area or per kg. dry soil) of the same numbers of nutrient atoms—e.g. potassium—in different potassium-bearing minerals. In this case the differences in effects, as measured by, for example, the dry-matter production, only depend on k_m, i.e. the nature of each mineral (the crystal lattice and the condition of the surface), if s in short-time intervals is not affected by t in different degrees for different minerals. In this way it is possible to get a satisfactory observation of the reaction of plants to, for example, potassium added in different potassium-bearing minerals.

Procedure and Results. Discussion

An experimental procedure which may be used in several cases is elucidated by the following example.

The fertilizing value of different copper minerals was determined in pot experiments by using barley (*Hordeum distichum*) and a sandy soil very deficient in copper. The soil had a fair content of acid humus originating from heather (*Calluna vulgaris*), which seems to have a special ability to fix copper in an almost unavailable state. Barley is very susceptible to copper deficiency. The growing season of barley is about 3 months, so it may be assumed that the relative surface areas of the different copper minerals (see below) were retained fairly well in the part of the growing season in which the absorption of copper mainly takes place, i.e. in May and the first half of June (Steenbjerg and Boken, 1943). The copper minerals were analysed mineralogically and chemically. The following minerals were used in the experiment:

Copper pyrites, $CuFeS_2$;

Bornite with copper glance;* bornite, Cu_5FeS_4; copper glance, Cu_2S;

Malachite, $CuCO_3.Cu(OH)_2$.

For further details of the experiment see Steenbjerg (1943*a*, *b*, 1951).

The possibility of calculating the number of copper atoms on the very surfaces of the minerals added to the soil (per kg. soil or per unit area of soil) is conditioned by the possibility of providing a figure—absolute or relative—for the size of the surface areas of the minerals. Two methods are usable, and the question whether to choose one or the other depends

* Called bornite in what follows.

on properties of the minerals used. By the pipette method, as modified by Andreasen and Berg (1925), a relative measure of the size of the surface areas (and of the numbers of copper atoms on the surfaces) is obtained, while the Brunauer, Emmett, and Teller method (or similar methods) as modified, for example, by Harkins and Jura (1944), may

TABLE 1

Minerals	Cu *added* (*g.*)	Cu *absorbed per pot* (*γ*)	% Cu *in the mineral* (*Low*)	*Added relative surface area cm.*²	$\frac{\text{Surface area} \times \% \text{ Cu}}{100}$ *Relative numbers of* Cu *atoms*	*g. dry matter per pot, grain+straw*
Basal dressing .	0	206	..	..	..	13·7
Copper pyrites II	0·57	215	18·0	15·6	2·8	20·2
The same .	2·85	245	18·0	77·6	14·0	26·1
Copper pyrites I	0·56	343	20·5	668	137	40·6
The same .	2·79	536	20·5	3,333	683	102·8
Bornite II .	0·52	230	58·9	6·7	4·0	16·4
The same .	2·59	264	58·9	34·3	20·2	23·7
Bornite I .	0·52	488	61·6	136	83·8	73·9
The same .	2·58	734	61·6	693	427	117·6
Malachite II .	0·50	442	51·4	8·6	4·4	32·0
The same .	2·50	577	51·4	43·2	22·2	60·5
Malachite I .	0·47	685	49·5	514	254	122·1
The same .	2·34	840	49·5	2,577	1,276	129·2
Copper sulphate	0·032	498	25·5	..	..	54·3
The same .	0·128	372	25·5	..	..	77·2
The same .	1·020	440	25·5	..	..	123·6

sometimes make it possible to obtain an absolute measure of the surface areas in question. The relative surface areas in cm.² listed in Table 1 are calculated on the basis of the analyses of fineness (Andreasen and Berg method) with reference to the results of the mineralogical analyses and the specific gravity of the various copper minerals. The calculations are further made on the assumption that the fragments (the particles) of the three minerals, copper pyrites, bornite, and malachite are cubes. In this connexion it should be noted that copper pyrites and bornite have no distinct cleavage, whereas malachite cleaves in layers in definite planes so that the surface per unit of volume after pulverization may really be somewhat larger in the case of this mineral than in the case of copper pyrites and bornite. Under the microscope it was not possible to observe any marked differences in form between the fragments of the three minerals. Assuming that the fragments on an average have nearly the same form, the ratio between the size of the surfaces of the various minerals must thus be independent of the question whether the fragments are calculated as cubes, pyramids, tetrahedra, or any other form. This fully applies to copper pyrites and bornite.

On the basis of the relative surface areas (expressed in cm.² in Table 1, column 5) the relative numbers of copper atoms are computed, which give a relative measure of the numbers of copper atoms situated on the fractured surfaces of the mineral particles. The relative numbers of Cu atoms are obtained by multiplying the relative surface area expressed in cm.² by the percentage content of copper in the mineral (Table 1, column 6). Thus it is assumed that the amount of copper atoms on the

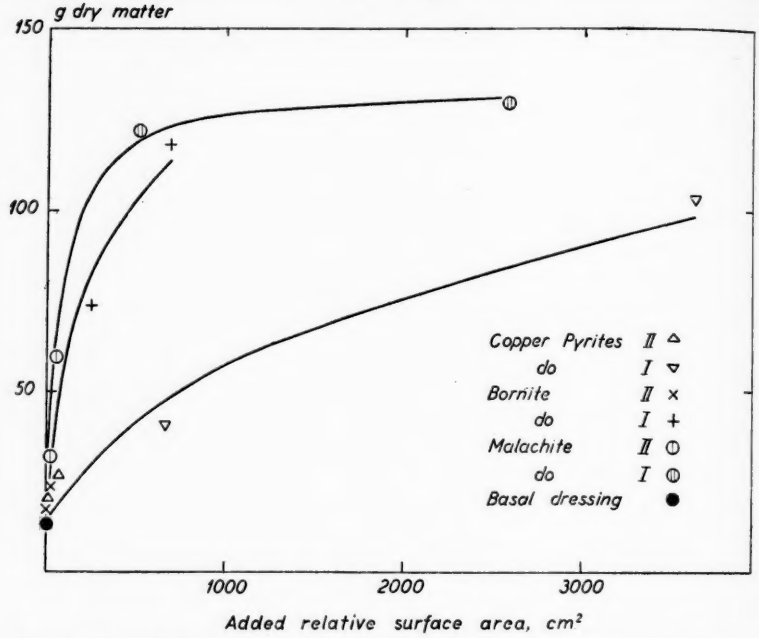

FIG. 1. The ratio between dry-matter production and added relative surface area.

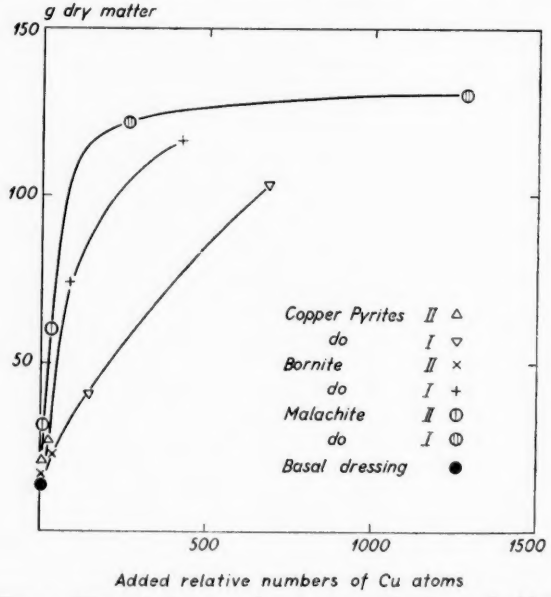

FIG. 2. The ratio between dry-matter production and added relative numbers of Cu atoms.

very surface of the mineral particles is proportional to the percentage copper content of the mineral. This way of calculating seems to be the only approximation possible with this material.

Fig. 1 shows graphically the ratio between grammes of dry matter per pot (grain+straw) and added relative surface area expressed in cm.^{2}; such curves may also be viewed as showing the ratio between yield and added increasing amounts of different copper minerals (expressed in units of weight) with the same particle size per unit of weight. It is seen in Fig. 1 that to obtain a dry-matter production of, for example, 90 g., the surface of copper pyrites must be about 3,000 cm.^{2} while the same production is obtained for bornite if the surface corresponds to about 300 cm.^{2} But further considerations along this line do not give a satisfactory picture of the relative value as measured by plants of these two copper minerals. A better picture of the relative rate at which the crystals of the two copper minerals disintegrate and release copper, and of how this disintegration or weathering influences plant growth, is obtained by computing the number of copper atoms (in this case the relative number) on the surface areas of the minerals used and then expressing the results graphically as shown in Fig. 2. It is seen that copper pyrites still weathers more slowly than bornite. A dry-matter production of 90 g. now corresponds to a relative number of Cu atoms of 150 in bornite, while the same dry-matter production is obtained by a relative number of Cu atoms of 550 in copper pyrites.

The relative fertilizing value (weathering rate with respect to release of copper atoms) of copper in the crystal lattice of copper pyrites as measured against copper in bornite is $\frac{150}{550} = 0{\cdot}272$, i.e. copper atoms are released 3·67 times as quickly from bornite as from copper pyrites as measured by barley under the conditions of the experiment.

The same result is obtained from Fig. 1 on the basis of the following considerations. The curve in Fig. 1 may be viewed as showing the ratio between yield and added increasing amounts of the different copper minerals expressed in units of weight, with the same particle size (surface area) per unit of weight; by considering the results in this way the size of the surface area is proportional to added quantities of weight, and so one surface area or another can be chosen as a unit of weight.

By a dry-matter production of 90 g. the following figures are obtained from Fig. 1:

	Surface area	*Units of weight*	% Cu	% Cu × *units of weight*
Copper pyrites	3,000	10	20·0	2·00
Bornite	300	1	61·6	0·616

Assuming as before (the surface area per unit weight is considered the same for both minerals) that the relative numbers of copper atoms on the surface areas are proportional to the percentage content of copper we obtain almost the same proportion, 0·616 : 2·00 = 0·308.

The same result is, of course, obtained if the graph showing the ratio between γ Cu absorbed (see column 3, Table 1) and added relative numbers of copper atoms is used for the computation. The small variations in the results found when various points on the different curves are used for the determination of the ratio in question may be eliminated by obtaining smooth curves, not by free hand as used here, but by some mathematical expression; this, however, is not of fundamental importance.

In order to try whether a similar result could be obtained by rather simple chemical tests the following investigations were made.

First the amount of copper dissolved in 25 per cent. hydrochloric acid (Van der Marel, 1947) was determined by weighing out 2·78 g. copper pyrites II and 0·55 g. bornite II, representing a relative number of copper atoms of 2·47 cm.^{2} (see Table 1) for both minerals. The minerals were extracted with 100 ml. hydrochloric acid for 1 hour. The following amounts of copper were dissolved: for copper pyrites II 1·32 mg. Cu per 100 ml. and for bornite 50·2 mg. Cu per 100 ml.

In the following determination of released copper per unit time the procedure was as follows. Amounts of copper minerals were weighed out representing the same relative number of copper atoms for both copper pyrites I and II and for bornite I and II. The shaking time in the different experiments varied from 10 minutes to 48 hours; an acetate-buffer solution at a pH value of 4·8 was used as the extracting agent. The results are shown in Table 2.

TABLE 2

Extraction of Copper Pyrites II and Bornite II with 100 ml. Acetate Buffer Solution at a pH-value of 4·8

Relative numbers of Cu atoms: 0·98 cm.^{2} equal to 1·11 g. copper pyrites II and 0·22 g. bornite II

Extraction time (hr.)	Cu *released from*	
	Copper pyrites	*Bornite*
1	165 γ Cu	65 γ Cu
3	170 ,,	76 ,,
6	186 ,,	114 ,,
12	205 ,,	178 ,,
24	272 ,,	340 ,,

When the results in Table 2 are plotted with the shaking time on the abscissa and the released copper on the ordinate, the graph shows that the ratio between the released copper and the shaking time is a constant for each mineral. Dividing the differential quotient for copper pyrites with that for bornite a value of about 0·38 is obtained, showing that under these conditions the copper atoms are released between 2 and 3 times as quickly from bornite as from copper pyrites. In other experiments with the fine copper minerals (I) nearly the same value, 0·39, was found. The order of magnitude of these results as compared with the result of the pot experiment is the same.

This rather good agreement was not expected and is surprising among others in view of the fact that the minerals tried, especially bornite with copper glance, have a complex crystallographic structure.

Summary

In order to use the growth of plants as an indicator of the release of nutrient elements from minerals (weathering) it is proposed to calculate the relative or, if possible, the absolute number of nutrient atoms on the very surface areas of the minerals found in or added to the soil.

During short-time periods the differences in the effect of the minerals as measured by the dry-matter production then depend only on the nature (crystal lattices and condition of the surfaces) of the minerals being weathered, other things being equal.

The results from pot experiments with copper minerals are plotted graphically with the dry-matter production on the ordinate, and the relative number of copper atoms on the abscissa. In this way it is possible to observe how plants react (dry-matter production) to the same number of Cu atoms added in different crystal lattices.

The general procedure and some experimental details are discussed.

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(*Received 7 October 1953*)

A REVIEW OF RECENT WORK ON SOIL ORGANIC MATTER. II

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MUCH useful information concerning soil organic matter has been obtained by non-isolative methods of investigation such as Waksman's system of proximate analysis. It is now generally realized, however, that such methods are of very limited and uncertain value, and that to achieve any real progress in the elucidation of the chemical nature of soil organic matter we must return to the isolative method of investigation used by Schreiner and Shorey at the beginning of the century. Greatly improved methods of characterizing organic substances are now available, but before they can be applied profitably to soil organic matter the latter must first be extracted and then suitably fractionated. It seems timely therefore to review recent work on the extraction and fractionation of soil organic matter and to discuss the information now available regarding a subject that has an important bearing on both of these problems, namely the interaction between the organic and inorganic colloids of soil.

Extraction of Soil Organic Matter

Although the lack of satisfactory methods of separating the organic complexes from the inorganic material of the soil has long been recognized, surprisingly little attention has been given to this problem. Caustic alkali has been used almost exclusively for the extraction of soil organic matter since 1786, when Achard [1] first employed it to isolate 'humic acid'. Generally a dilute (0·5 M) solution of sodium, potassium, or ammonium hydroxide is used, but more concentrated solutions have often been employed. Consideration of the possibility that caustic alkali may seriously affect the physico-chemical properties of soil organic matter led Bremner and Lees [2] to seek milder methods of extraction. With this object they surveyed the extracting powers of various neutral reagents, particularly the sodium salts of organic and inorganic acids. Sodium pyrophosphate, sodium oxalate, sodium fluoride, and sodium citrate were found to be the most effective of the reagents tested, pyrophosphate being the most generally useful, but all of these salts extracted less organic matter than caustic alkali, especially from mineral soils. The results obtained in this work and in a previous investigation [3] indicated that soil organic matter is intimately associated with metallic cations and that its solubility in neutral reagents is largely determined by the nature and extent of this association. The efficiency of a neutral salt extractant would appear to depend on the ability of its anion to remove interfering metals either as insoluble precipitates or as soluble co-ordination complexes. For efficient extraction the cation of the neutral salt must be sodium, potassium, lithium, or ammonium since other cations cause precipitation of the organic matter. The efficiency of 'calcium-masking'

reagents (oxalate, citrate, &c.) indicates that calcium is one of the chief interferents in the extraction of organic matter from soil.

According to Aleshin and Zhupakhina [4], sodium oxalate peptizes mainly humic matter saturated with calcium, whereas sodium hydroxide peptizes humic matter saturated with hydrogen. Remezov [5], however, considers that sodium hydroxide and sodium fluoride extract humates combined with minerals.

Chaminade [6, 7] found that oxygen has an important effect on the extraction of humic matter from soil by alkali, the amount extracted in the presence of oxygen being as much as three times the amount extracted in a hydrogen atmosphere. This led him to a study of the extractive powers of neutral salts from which he concluded that the humic colloids of soil can be estimated by decalcifying the soil with dilute acid, extracting with 3 per cent. ammonium oxalate, and then determining the humic matter in the extract by a permanganate method. Results obtained by this method were found to be identical with those obtained when extraction was carried out by means of alkali in an atmosphere of hydrogen. Chaminade found that the amount extracted by alkali in the presence of oxygen was dependent upon the concentration of the alkali and the time of extraction, whereas it was independent of these factors in the absence of oxygen. Bremner and Lees [2] also noted that the amount of organic matter extracted by alkali in the presence of oxygen depended upon the alkali concentration and the time of extraction, but Bremner [8] could not confirm Chaminade's finding that alkali extracts much more organic matter in the presence than in the absence of oxygen. Using mineral soils he found that oxygen had no significant effect on extraction by alkali. Bremner [9] also compared the amounts of carbon and nitrogen extracted from various soils by sodium hydroxide, sodium carbonate, sodium pyrophosphate, and sodium fluoride and found that under the influence of any one of these reagents organic carbon was dissolved only along with, and in proportion to, organic nitrogen. However, the relative proportions of carbon and nitrogen extracted were found to vary with both the soil and the extractant, sodium hydroxide extracting more nitrogen in relation to carbon than did the milder reagents.

Further investigations on the extractive powers of neutral salts have been reported by Hamy and Leroy [10, 11]. They compared the ammonium salts of organic acids and found that oxalate, malonate, and salicylate were much more efficient than succinate, adipate, maleate, trichloracetate, acetate, or phthalate. Diphenols were effective extractants. They also studied the effect of the cation in neutral salt extraction by comparing the efficiencies of solutions of the lithium, sodium, ammonium, potassium, and magnesium salts of malonic acid and found that the extractive powers of the solutions decreased in the order given. They point out that the most effective neutral extractants, e.g. oxalate, tartrate, citrate, malonate, salicylate, are those capable of forming complexes with iron.

Martin [12] recommends a sodium fluoride-sodium borate-boric acid buffer of pH 9 for the extraction of humic substances.

A considerable fraction (20–40 per cent.) of soil organic matter cannot

be extracted by alkali. According to Khan [13] this alkali-insoluble ('humin') fraction can be brought into solution by repeated alternate treatments of the soil with sulphuric acid and sodium hydroxide (0·1 N). At least 15 acid-alkali treatments were found to be required, the concentration of the acid being increased from 7 to 25 per cent. in the process. It seems unlikely that this method of extraction will find much application since organic matter thus dissolved is hardly likely to bear much resemblance to the original material.

It is clear from this short review that no satisfactory method of extracting the organic complexes of soil is yet available. Several useful neutral extractants have been introduced, but their virtue of mildness is offset by the fact that they extract considerably less than the classical reagent. It seems likely therefore that most workers will continue to prefer the more complete extraction by caustic alkali even though it is achieved at the cost of some damage to the organic complexes.

Interaction of Organic and Inorganic Soil Colloids

The difficulties encountered in the extraction of organic matter from soil serve to remind us that the separation of soil colloids into organic and inorganic components is easier on paper than in the laboratory and that interaction between the clay and humus colloids of soil is highly probable. Evidence of such interaction is now substantial, if indirect, and several papers dealing with clay-humus complexes have recently appeared. For example, Tiulin [14–20] has reported that the clay-humus colloids of soil can be separated into two main groups by fractional peptization. Group I consists of colloids which, when saturated with sodium ions, are dispersed in water. These colloids are electro-negatively charged and have a high base-exchange capacity. Group II consists of colloids which, after removal of Group I, are dispersed in weak alkali before and after treatment with dilute acid. This group is iso-electric or weakly electro-negative and has a low base-exchange capacity. Further fractionations of these groups were effected. Tiulin considers that the organic matter in the Group I colloids is very active, being merely adsorbed on the gel surface, whereas that in the Group II colloids is inactive, being firmly bound in the interior of the gel particles. He states that the Group I colloids are the main carriers of available nitrogen and phosphorus and that they promote a stable crumb structure. Tiulin found that the ratio of Group I to Group II colloids is very high in chernozems and low in podzols and suggested that this ratio furnishes a guide to the soil's inherent fertility. Support for this suggestion was provided by the finding that when flax was grown in sand cultures, addition of increasing quantities of soil in which the ratio of Group I to Group II colloids was high increased the yields whereas addition of soils with low ratios decreased the yields [21]. Roots grown in soils with a high proportion of Group II colloids were found to be coarser and less branched and to have fewer root-hairs than those grown in soils rich in Group I gels. Further support came from the work of Vinokurov and Koloskova [22], who found that the improvement in the fertility of podzol

soils brought about by mixing the A and B_1 horizons is accompanied by an increase in the quantity of Group I colloids in the cultivated layer.

Other Russian workers [23–27] have investigated Tiulin's method of fractionation, but outside Russia only Atkinson and his associates [28–30] appear to have used the method. They applied it to Canadian soils and obtained results similar to those of Tiulin. For example, they found highly significant relationships between the quantities of Group I colloids and the yields of barley and clover obtained from seven Canadian soils [29]. In more recent work Atkinson and his co-workers have compared the chemical properties of fractions isolated from soils by the Tiulin method [31–33]. They could find no chemical differences between the fractions that would account for Group I colloids being of greater importance than Group II colloids from the soil-fertility standpoint.

Remezov [5] considers that N sodium chloride extracts only 'free' humates, being too weak to hydrolyse organo-mineral complexes, whereas sodium hydroxide (0·1 N) and sodium fluoride (0·2 N) are able to dissolve humates combined with minerals.

Springer [34] considers that the natural fertility of the chernozems is associated with the great stability of their clay-humus complexes. Meyer [35, 36] succeeded in preparing from artificial permutites and humic acids complexes that were very similar in stability and other properties to the natural clay-humus complexes of chernozems. He considers that in both the organic component forms an integral part of the structure and is not, as Tiulin believes, merely superficially adsorbed. Meyer was unable to prepare stable chernozem-like complexes from montmorillonitic clays and humic acids, but concluded that such complexes arise in nature by formation *in statu nascendi*, i.e. by interaction of humic acids formed by decomposition of plant materials with montmorillonitic or micaceous clays formed simultaneously by the weathering of primary rock minerals.

Gel'tser [37–42] holds such definite views about the importance of clay-humus interaction in the development of soil structure that she defines humus as that fraction of the organic colloids of soil which is capable of forming stable aggregates with the inorganic colloids of the soil. According to Gel'tser, this fraction is not of plant origin but is the product of the autolysis of the bodies of bacteria which have developed on the hyphae of the fungi which carry out the initial processes of the decomposition of plant residues. She prepared such microbial products *in vitro* and showed that they were resistant to further microbial decomposition and possessed a remarkable ability to cement clay particles into aggregates. An excellent review of Gel'tser's work and her views on the role of clay-humus complexes in the development of soil structure and fertility has been published [43].

Khan [44] studied the absorption of ammonium humate by askanite, kaolin, orthoclase, microcline, and mica, and deduced from the results that there were two types of absorption. In one (kaolin) humic acid was absorbed on the crystal surface: in the other (askanite) it entered the interior of the crystal. He later extended this investigation to include muscovite, bentonite, and gumbrin and found that the montmorillonite

minerals (askanite, gumbrin, bentonite) absorbed much more humic acid than the others, askanite absorbing most and kaolin least [45, 46]. Absorption was greatest at a neutral or slightly acid reaction. He also found that minerals saturated with iron or aluminium ions absorbed much more humic acid than the same minerals saturated with hydrogen or calcium ions. A particularly interesting result of Khan's work was his finding that much of the humic acid absorbed by clay minerals cannot be extracted by 0·1 N sodium hydroxide [46].

Jung [47] found that whereas the base-exchange capacity of montmorillonite-humate complexes was equal to the sum of the exchange capacities of the components, the exchange capacity of complexes formed by interaction between the same humate and a soil colloid was less than the combined exchange capacities of the components. This reduction he attributed to the action of sesquioxides, which, he considers, play an important role in binding clay and humus colloids.

Many other studies on the interaction between the organic and inorganic colloids of soil have been reported [48–60], and a great variety of methods, including viscosimetric, X-ray, and electron-microscopic techniques have now been applied to the problem, but no clear picture regarding the nature of the interaction is yet apparent. The great difficulty in all such investigations is the lack of satisfactory information regarding the structure of the organic colloids. Until such information is obtained any theory regarding the nature of clay-humus complexes must be regarded as speculation.

Whatever the nature of clay-humus complexes, there is now substantial evidence to suggest that the clay colloids of soil may play an important role in stabilizing soil organic matter against biological attack. Reference to such evidence was made in Part I of this review, when the work of Ensminger and Gieseking, Bower, and Allison, Sherman and Pinck was discussed [61]. Further evidence of the stabilizing effect of clays has since appeared. For example, Pinck and Allison [62] have shown that the rate of decomposition of gelatin by soil micro-organisms is much reduced if the gelatin is mixed with bentonite, and still further reduced if the gelatin is in the form of a complex with bentonite. Erickson [63] has confirmed Ensminger and Gieseking's finding that proteins are more resistant to enzymatic attack when adsorbed on clays. Goring and Bartholomew [64, 65] have shown that clays retard phosphorus mineralization from microbial tissue and Mortland and Gieseking [66] have demonstrated that the enzymatic hydrolysis of organic phosphorus compounds (phytin, lecithin, &c.) is also inhibited by clay minerals. In all these investigations the protective action of bentonite was found to be much greater than that of kaolinite.

The interaction of clay and humus colloids deserves greater attention in the future. Apart from the fact that it may have an important bearing on the structure and fertility of soils and on the maintenance of soil organic matter, this interaction undoubtedly contributes to the difficulties experienced in separating the organic and inorganic soil colloids. Any advance in our knowledge of the mechanism of the interaction may therefore lead to improvements in methods of extracting organic matter from soil.

Fractionation of Soil Organic Matter

Although much of the earlier work on soil organic matter was concerned with the fractionation of the organic complexes, little attention has been given to this problem in recent years except by German workers. The characteristic feature of their work has been the use made of acetyl bromide as a reagent for the separation of humified and unhumified material. They consider that this reagent dissolves all undecomposed or partly decomposed plant materials (including lignin) without dissolving any of the humified material ('true' humus). Springer [67] has used a mixture of acetic acid, acetic anhydride, and sulphuric acid for the same purpose. In the absence of any criteria of humification the separation would appear to be quite arbitrary. It is presumably based on susceptibility to acetylation. Various complicated methods of characterizing different types of organic matter have been devised by the German school, but they are so empirical that they have aroused little interest outside Germany. A very useful review of this work has been published in *Soils and Fertilizers* [68].

Lein [69] applied the method of centrifugal separation of minerals with heavy liquids to soil and examined the fractions obtained by microscopic and X-ray methods. He concluded that the lightest fraction contained 'free' organic matter consisting of partly decomposed plant residues, humates, and humic acids and that the heaviest fraction contained fulvic-like complexes combined with or absorbed on mineral substances. He found that the intermediate fraction contained the most firmly bound organic matter and suggested that this consisted of ester-like complexes of humic and fulvic acids. Hénin and Turc [70–72] have described a similar density method of fractionating soil organic matter. Using mixtures of benzene and bromoform they distinguished two main fractions. One (the lighter) consists mainly of plant residues and has a high C/N ratio: the other is closely bound to the mineral matter and has a low C/N ratio.

Although remarkable separations of organic substances have been accomplished in recent years by the use of chromatographic methods of fractionation, only Hock [73] and Forsyth [74] appear to have attempted to apply such methods to soil organic matter. Hock [73] showed that solutions of humic, fulvic, and hymatomelanic acids gave different types of chromatograms when passed through a column of alumina and concluded that this method could be used for the physical separation of humus fractions. Forsyth [74] found that the fulvic fraction of soil extracts could be separated into four parts by a selective-adsorption technique. This separation was achieved by passing the fulvic solution through a pad of charcoal, the filtrate and washings (with 0·1 N hydrochloric acid) forming fraction A. Fractions B, C, and D were then obtained by eluting the charcoal with 90 per cent. acetone, distilled water, and 0·5 N sodium hydroxide, respectively. A preliminary chemical examination of the fractions distinguished by this method indicated that fraction A contained simple organic substances such as amino-acids and sugars, and that phenolic glycosides were present in fraction B. Fraction

C was found to contain polysaccharides containing uronic groups. The results obtained in a further investigation of these polysaccharides [75] were discussed in Part I of this review. Fraction D was found to give positive tests for pentose sugars and to be rich in nitrogen and phosphorus.

These results, taken with the failure of attempts to achieve useful fractionations of humus by chemical methods, suggest that the time is now ripe for an intensive application of modern chromatographic methods of fractionation. The application of such methods is not likely to prove simple, but effort expended in this direction should eventually prove more profitable than that given to any further attempts to separate humified and unhumified material. Other physical methods of fractionation, such as electrophoresis, may also prove of value. In this connexion attention may be drawn to recent work by Martin and his associates [76, 77]. They subjected organic matter extracted from Brookston clay by means of neutral sodium pyrophosphate to electrophoresis and deduced from the results that it consisted of one main component with a second present in small concentration. Similarly Bremner and Arnold [78] found that when a soil humic-acid preparation was examined by the method of paper electrophoresis it behaved as if it consisted of only one component. These results suggest that the electrophoretic technique has definite limitations as a method for the fractionation of soil organic matter. Several of the difficulties involved in the application of the technique to soil organic colloids have been discussed by Stevenson, Marks, Varner, and Martin [77].

The classical method of fractionation with alkali and acid is still used as a preliminary to most chemical investigations on soil organic matter. Recent work on the fractions distinguished by this method are discussed below.

The Humic and Fulvic Fractions of Soil Organic Matter

No generally accepted definition of the term 'humic fraction' is available, and in a review of recent literature in which the term is used in different senses by different authors it would be futile to attempt a definition. It may be said, however, that although the term is generally reserved for that fraction of soil organic matter which is soluble in alkali but insoluble in acid or alcohol, its meaning is frequently broadened to include any fraction of soil organic matter that is soluble in alkaline or neutral reagents and is insoluble in acid. The terms 'humic fraction', 'humic complex', and 'humic acid' are used synonymously.

The literature concerning the humic fraction of soil organic matter is so extensive that no attempt can be made here to review work carried out on the subject before 1940. For the purposes of this review, however, it may be said that by 1938, when Waksman's [79] comprehensive survey of the literature was published, the lignin theory of the origin of humic acids and the ligno-protein theory of their nature were generally accepted. Most of the work carried out since that time has been concerned in some way with these theories. It consists largely of studies on the changes undergone by lignin in its conversion to humic material and on the

chemical nature of humic nitrogen. Gillam [80], for example, studied three humic-acid preparations isolated from prairie, chestnut, and chernozem soils by determining their acetyl and methoxyl contents, their base-exchange capacities up to pH 7, and their buffer curves before and after methylation and acetylation, and compared the results with those obtained when lignin preparations were similarly investigated. From the data thus obtained he concluded that if humic acids are derived from lignins, their formation involves a gain in carboxylic groups and a loss of methoxyl groups and of hydroxyl groups that can be methylated. He found that the three humic preparations examined were very similar in their chemical and physical properties and concluded from his investigations that humic acids are formed by combination between a slightly modified lignin complex and protein-like material.

Gillam's work was extended by Forsyth [81], who argued that humic acids as normally obtained are always contaminated with varying amounts of co-precipitated and adsorbed material. He purified his preparations by subjecting them to hydrolysis with dilute acid (2 per cent. hydrochloric acid for 4 hours under reflux), a procedure which he claimed removed extraneous material but did not affect true humic acids, and subjected the products to ultimate (carbon, hydrogen, nitrogen, ash) and group (acetyl, methoxyl, hydroxyl, carboxyl) analysis. From these analyses he deduced that while the various humic acids have similar molecular structures the number and kind of reactive groups depend upon the conditions and length of time under which the humus is formed. 'Humification' appeared to involve both hydrolysis and oxidation of the original lignin. Forsyth found that the nitrogen contents of his purified preparations were not significantly affected when the preparations were methylated, esterified, and acetylated by somewhat vigorous procedures and concluded that humic nitrogen could not be in the form of protein and must form part of the molecular structure. This conclusion is not supported, however, by results obtained recently at Rothamsted when the specific ninhydrin method was used to determine the amino-acid contents of acid hydrolysates of various humic acids as normally prepared and of the same preparations after purification by the acid-hydrolysis procedure [82]. These results showed that with humic acids extracted in the usual way with alkali, 40–45 per cent. of the nitrogen in the unpurified preparations and 27–34 per cent. of the nitrogen in the purified preparations was liberated as α-amino nitrogen by hydrolysis with 6N hydrochloric acid and must therefore have been in protein-like combination. The amino-acid composition of this protein material has been studied by paper chromatography [82].

Other investigations on the chemical nature of humic nitrogen have been reported by Dragunov, Zhelokhovtseva, and Strelkova [83] and by Atkinson, Sowden, Parker, and Davidson [31, 33, 84]. Dragunov and his co-workers [83] studied the effect of acid hydrolysis (5 per cent. hydrochloric acid for 2½ hours under reflux) on chernozem, podzol, and peat humic acids and found that 40–60 per cent. of the nitrogen in the preparations was liberated by acid hydrolysis, mainly in the form of mono-amino acids. Atkinson and his associates [31, 33, 84] compared

the properties of humate fractions separated from Group I and Group II colloids obtained by Tiulin's method of fractionation and found that they were very similar in nitrogen distribution and amino-acid composition. However, their nitrogen distribution after hydrolysis was found to differ considerably from that of protein material. They also showed that when such humate fractions were subjected to a procedure commonly employed for the separation of lignin from plant material the 'lignins' obtained differed in many respects from plant lignin. They had a low methoxyl content, a high nitrogen content, and were soluble in water. However, their ultraviolet absorption spectra had characteristics similar to those of lignin and related compounds. These results led them to conclude that the humates examined were not simple lignoprotein complexes and that a considerable proportion of their nitrogen was not in the form of protein [31].

Support for the view that humic acids are formed by processes involving oxidation of the plant lignins entering the soil has been provided by the finding that oxidized lignins have several of the properties of humic acids. For example, it has been found that products formed by autoxidation of lignin in alkaline solution and other types of oxidized lignins resemble humic acids in that they have a higher base-exchange capacity [85–87] and disperse at a lower pH value [88] than unoxidized lignins. Mattson and Koutler-Andersson [89, 90] found that if the autoxidation of lignin is carried out in ammonium hydroxide the product contains a considerable percentage of chemically stable nitrogen. They also found that lignin was able to fix ammonia in a non-exchangeable form under soil conditions [90], and that the titration curves of products obtained by alkaline autoxidation of lignin were identical to those of the acidoids present in humus of the chernozem type [91]. These and other observations have led them to conclude that the humic complexes of soil are derived from lignin by autoxidation and ammonia fixation.

Esh and Guha-Sircar [92] studied the chemical properties of soil and peat humic acids which they obtained by a rather drastic procedure involving the use of hot acetyl bromide, and found that the preparations had low methoxyl contents, contained no acetyl or methylenedioxy groups, and did not evolve appreciable quantities of furfuraldehyde when boiled with 12 per cent. hydrochloric acid. They also studied the oxidation of a commercial peat humic acid with hydrogen peroxide, hot alkali, and chlorine dioxide, and showed that potash fusion of this preparation followed by methylation and permanganate oxidation yielded veratric, veratroylformic, and isohemipinic acids, products that are obtained when lignin is submitted to the same process [93]. Dragunov, Zhelokhovtseva, and Strelkova [94] and Botteri [95] have also shown that potash fusion of humic-acid preparations yields products similar to those obtained with lignin, e.g. pyrocatechol and protocatechuic acid.

Lein [96] found that complexes formed of lignin and protein had not, as stated by Waksman, a higher exchange capacity than the sum of the components, and concluded that such complexes are not the forerunners of natural humic acids.

Natkina [97] found considerable differences between humic acids

isolated from chernozem and podzol soils and deduced from these that the humic acid from the podzol was considerably younger than that from the chernozem, the processes of oxidation and dehydration being considerably more advanced in the latter.

Rydalevskaia and Tishchenko [98] and Dragunov, Zhelokhovtseva, and Strelkova [94] have compared the properties of chernozem, podzol, and peat humic acids. Rydalevskaia and Tishchenko [98] determined their exchange capacities before and after methylation and deduced from the results that both carboxyl and hydroxyl groups took part in cation exchange. At all pH values the exchange capacities of the chernozem and podzol humic acids were greater than that of the peat humic acid. Dragunov and his associates [94] found that the preparations were remarkably similar in their behaviour towards methylation with methanol saturated with hydrochloric acid, but that marked differences between the soil humic acids were revealed by methylation with dimethyl sulphate and diazomethane.

Tiurin [99] regards the formation of humic acid from lignin as an enzymatic oxidation accompanying the breakdown of lignocellulose in plant materials. He suggests that in soil humic and fulvic acids are united by an ester linkage which is unaffected by acids but readily hydrolysed by alkalis [100], and that the humins (i.e. acid- and alkali-insoluble organic complexes) represent polymerized, ester-like products of humic and fulvic acids [101]. However, there is no evidence to indicate that either of these suggestions deserve serious consideration. It is sufficient by way of criticism to point out that the organic matter extracted from soil by neutral reagents, which are hardly likely to affect an ester linkage, is separable into humic and fulvic fractions similar to those found in alkali extracts.

Kononova [102–6] has studied the humification of plant residues (clover, lucerne, &c.) by combining histological microscopic investigations of decomposition with simultaneous chemical analysis of the decomposing material. She found that the first stage of decomposition is effected by fungi which attack the simple carbohydrates and part of the protein and cellulose in the medullary rays, cambium, and cortex. No humic material is formed during this initial decomposition. The second stage is characterized by the decomposition of the cellulose of the xylem by aerobic myxobacteria and by the formation of brown humic matter. During these two stages the lignified tissue is scarcely affected. Kononova considers that these results throw doubt on the lignin theory of the origin of humic acids and suggest that humic matter is produced by the activities of cellulose-decomposing myxobacteria before the lignin in plant materials has begun to decompose. In more recent papers [107, 108] she emphasizes the role of cellulose myxobacteria in the humification of plant residues and states that humic acids are formed at the time of intense cellulose decomposition by the interaction of organic nitrogen compounds in the myxobacterial protoplasm with soluble polyphenols (tannins, lignin precursors, &c.), the reaction being catalysed by oxidative enzymes of the myxobacteria. Kononova found that the brown substances formed by the activities of cellulose-

decomposing myxobacteria were very effective in promoting the formation of water-stable aggregates in soil. In many respects, therefore, her work has substantiated the views of Gel'tser discussed above.

Springer [109] considers that there are two distinct types of 'true' humic acid (insoluble in acetyl bromide) characterized by the different colours of their alkaline solutions, namely brown and grey humic acid. A method for the separation of these acids has been described by Meyer [110].

Numerous X-ray and electron-microscope studies on the structure of humic acids have been reported, but little useful information has emerged from these investigations and they have led to considerable diversity of opinion. Thus Sedletsky and his co-workers [55, 111–13] have concluded from X-ray, electron-microscope, and thermal investigations that humic acids from soils and peats are identical in constitution and have a crystalline structure that is basically aromatic (graphite lattice). Gemmerling and Zyrin [114] have deduced from their X-ray studies that humic acids from different soils are not identical, but that there is a crystalline component which does not vary much from soil to soil. On the other hand, Jung [115], Gorbunov [116], Flaig and Beutelspacher [59], Botteri [95], and Schuffelen and Bolt [117] have all been unable to detect signs of crystal structure in humic acids by X-ray or electron-microscope examination. According to Gorbunov [116], Debye rings are apparent only in samples of humic acids containing more than 2 per cent. of mineral salts, and the diffuse rings sometimes obtained with humic-acid preparations are caused by intramolecular diffraction.

A novel feature of recent German and Russian work on humic acids has been the use made of their optical properties for purposes of comparison and characterization [4, 118–23]. For example, Frömel [118] compared the absorption of light by humic acids from various sources and deduced from this and from a comparison of their adsorptive properties that all the preparations examined had similar chemical structures. Kononova, Pankova, and Belchikova [119] measured the absorption spectra of humic acids from manured and unmanured podzol and chernozem soils and concluded that there was no significant difference between the humic acids of unmanured and manured soil but that podzol humic acid differed markedly from chernozem humic acid. Aleshin and Zhupakhina [4] studied the absorption of light by sodium-hydroxide and sodium-oxalate extracts of various soils and deduced that the humic acids in these extracts had identical optical properties. Scheffer and his associates [121–3] have compared the structures of artificial, microbial, and soil humic acids by absorption spectrography (see below) and claim that the presence in soil of grey and brown humic acids, and their constitutional differences, are revealed by this technique.

Many other investigations on the properties of the humic fraction of soil have been reported, but limitations of space prevent their discussion here. However, attention may be drawn to the work of Forsyth and Fraser [124] who found that the colloidal properties of acid-precipitated humic-acid gels are destroyed if they are frozen solid in the presence of electrolytes, and that because the humic precipitates lose their water-holding

capacity and adsorptive power in this process they can subsequently be readily filtered, washed free from soluble contaminants, and dried by standard methods. This technique should prove of considerable practical value in future investigations on soil humic acids.

Considerable attention has been given in recent years to the properties of humic substances produced outside the soil either by chemical synthesis in the laboratory or by the activities of pure cultures of micro-organisms. Laatsch [125], for example, has shown that products resembling humic acids can be prepared by oxidizing quinone, especially in the presence of ammonia, and that the more oxygen and ammonia absorbed the more closely does the product resemble natural humic material. Reference may be made here to Mattson and Koutler-Andersson's observation that lignin fixes ammonia irreversibly during autoxidation and that the more oxygen and ammonia absorbed the more resistant to chemical attack and the less soluble in acetyl bromide is the product [90]. Laatsch and his co-workers [125–8] have also shown that soil micro-organisms, especially fungi and actinomycetes, produce substances resembling humic acids, and have concluded from their investigations that humic acids of high nitrogen content occur in soil as metabolic and autolysis products of micro-organisms. They suggest that many micro-organisms produce quinone derivatives *in vivo* and that these react with amino compounds to give humic acids. The nitrogen present in humic substances produced by micro-organisms and by oxidation of quinone in the presence of ammonia has been investigated [127, 128].

Using ultraviolet spectroscopy, Scheffer and his associates [122, 123] found that the dark brown substances present in autolysates of *Aspergillus niger* and of an actinomycete strain from a calcareous soil had structures very similar to that of the grey humic acid of soil and that the quinone structure of the actinomycete humic acid closely resembled that of an artificially formed quinone humic acid. They postulated that this actinomycete humic acid was formed by a mechanism involving condensation or polymerization of a quinoid metabolic product of the micro-organism under slightly alkaline conditions.

Von Plotho [129, 130] studied the formation of humic substances by various fungi, actinomycetes, and bacteria and found that it was affected by the form of nitrogen supplied to the culture solution. Flaig and his co-workers [131–3] have confirmed this result with streptomycetes and have classified streptomycete strains into groups according to the nitrogen source with which they react to produce humic substances.

According to Küster [134], the red pigments of *Aspergillus niger* and streptomycetes represent intermediates in the formation of humus-like substances.

Flaig [135] has studied the formation of dark brown acid-precipitable substances by oxidation of hydroquinone and catechol with molecular oxygen in alkaline solution and has presented a scheme of the reactions involved. Optimum production of these phenol-humic acids was found to occur at pH 7–8. Resorcinol did not react under these conditions. Flaig found that when hydroquinone was oxidized in an ammonium-hydroxide solution of about pH 10 the product contained about 6 per

cent. of heterocyclically bound nitrogen that was resistant to distillation with concentrated alkali. No difference between these synthetic phenol-humic acids and natural humic acids could be detected by electron microscopy; neither showed a crystalline structure [59]. Further investigations on the formation of humic substances by oxidation of hydroquinone have been carried out by Cornec and Brusset [136, 137] and Flaig and Schulze [138].

Treccani Benetti and Schiesser [139] have reported that some flavobacteria able to utilize benzoic acid and various phenolic compounds as sole source of carbon produce dark brown substances resembling soil humic acids when sodium salts of organic acids are added to the nutrient medium. Pochon, Wang, and Tchan [140–2] found that the properties of the black substances produced by the action of *Azotobacter* on sodium benzoate were remarkably similar to those of the humic complexes of soil, and concluded that one mechanism of humic-acid formation must be the oxidation of benzoic acid and related substances normally present in soil.

Enders [143, 147] believes that the formation of humic substances in soil has much in common with the formation of melanoidins during the manufacture of beer and has advanced the theory that both humic acids and melanoidins are formed by condensation of amino-acids and methyl glyoxal produced by autolysis of micro-organisms. He postulates that when the metabolic processes of micro-organisms are disturbed by autolysis the decomposition products of proteins (amino-acids) and carbohydrates (methyl glyoxal) are no longer used up in normal metabolism and condense to form humic substances. Support for this theory has been provided by the finding that methyl glyoxal-amino acid condensation products have properties similar to those of soil humic acids and by the detection of methyl glyoxal in soils, in humified materials from various sources, and in products of autolysis of micro-organisms [143–9]. Further support has been provided by Schuffelen and Bolt [117], who found that the C/N ratios, base-exchange capacities, and titration curves of products obtained by condensing glycine with methyl glyoxal were similar to those of 'dalgrond' humus isolated from reclaimed peat soil by extraction with ammonia.

In concluding this section, and by way of summary, it may be said that there are now two distinct theories regarding the origin of the humic substances of soil. One is that they are formed by the alteration of plant lignins entering the soil, the other that they are products synthesized by, or formed by autolysis of, soil micro-organisms. The former is represented by the ligno-protein theory of Waksman and the lignin-ammonia theory of Mattson and Koutler-Andersson, the latter by the theories of Gel'tser, Kononova, Laatsch, and Enders. There is good evidence for both of these theories, but the chemical nature of the humic fraction of soil remains obscure. The available information refers mainly to the functional (side) groups, very little being known about the chemical nature of the 'nucleus'. In this respect the chemistry of the humic fraction is in much the same state as lignin chemistry, and the indications are that progress in the elucidation of the chemical nature of the humic

complexes is dependent upon further advances in the chemistry of lignin.

The fulvic (i.e. alkali-soluble, acid-soluble) fraction of soil organic matter has received much less attention than the humic fraction and very little is known about its chemical nature. Forsyth's [74] work on the fulvic fraction has already been discussed in the section on fractionation. Other investigations have been reported by Ponomareva and Tiurin. Ponomareva [150] studied the properties of fulvic acids isolated from soil in the form of their ammonium salts and found that they could be separated into fractions precipitated and not precipitated by calcium or barium hydroxide. The latter fraction was the lighter in colour and contained the greater percentage of carbon. Ponomareva also prepared free fulvic acids by electrodialysis of ammonium, calcium, and barium fulvates and determined their elementary constitution, base-absorbing capacity, and equivalent weight. The latter was found to be about 160. However, Tiurin [100] has reported that fulvic acids are nitrogenous complexes of equivalent weight about 300. Both Tiurin [151] and Ponomareva [152] have obtained results which suggest that substances present in the fulvic fraction may effect the mobilization of sesquioxides during podzolization. Bremner [82] has shown that at least 20–30 per cent. of fulvic nitrogen is in the form of protein and has studied the amino-acid composition of this protein material. Recent work on the organic phosphorus of soil, discussed in Part I of this review, has shown that the fulvic fraction of soil extracts contains inositol phosphates and nucleic-acid derivatives, and that a considerable fraction of its nitrogen must be in the form of nucleic acids or nucleotides.

The Lignin-derived Fraction of Soil Organic Matter

It is generally believed that a substantial fraction of soil organic matter is in the form of lignin or lignin-derived material. Evidence for this has been deduced from studies on the biological decomposition of plant materials, which indicate that lignin is highly resistant to microbial attack, from the presence of methoxyl groups in humus, from the resistance of a considerable fraction (30–50 per cent.) of soil organic matter to cold strong acids, and from the isolation of aromatic phenolic compounds such as protocatechuic acid and pyrocatechol after fusion of soil organic matter with alkali. This evidence, though suggestive, is open to criticism on the grounds that it is largely presumptive, not direct. Attempts to obtain more direct evidence have been hindered in the past by the inadequacy of information regarding the constitution of lignin and by the lack of satisfactory methods for its separation and identification. In recent years, however, very considerable advances in the chemistry of lignin have been made and many new methods of isolating and characterizing lignin have been developed. The application of some of these methods to soil organic matter is discussed below.

It is now established that lignin from different sources is not homogeneous. For example, clear differences are recognizable between the lignins of deciduous and coniferous woods. Norman and Peevy [153] reasoned that the lignin-derived fraction of soil organic matter may also

differ according to its source and that these differences may be revealed by the results obtained on oxidation of soil organic matter with hypoiodite, a reaction which they considered to be primarily one in which the lignin-derived fraction of soil organic matter is involved. Considerable differences in the susceptibility of the organic matter to this reagent were found between soils and within the several horizons of soil profiles. The hypoiodite method of Norman and Peevy has been investigated and modified by both Norman [154] and Moodie [155], and has been used to establish differences between the organic matter of different surface soils and within the several horizons of profiles [153, 154, 156], to determine the effect of delignifying procedures on soil organic matter [157], and to follow the alteration of lignin [158] and the changes in amount of hypoiodite-oxidizable material [159] during the biological decomposition of plant substances. However, it is very difficult to interpret the results obtained by this method since no definite information regarding the nature of the reaction between hypoiodite and soil organic matter is available. Norman [154] and Moodie [155] have obtained results which suggest that the phenolic-hydroxyl group of lignin-derived material is the probable point of attack, but until more is known about the reaction the hypoiodite procedure must be regarded as an entirely empirical method with all the limitations and shortcomings of such methods.

Much of the progress made in recent work on lignin has been due to the development of new methods of isolating lignin from plant materials. Norman and Moody [157] studied the effect of a number of these methods upon the organic matter of two surface soils by determining the reduction in organic carbon and the change in susceptibility to hypoiodite oxidation. They found that although the application of delignifying procedures brought about extensive removal of organic carbon, the behaviour of the residues indicated that the grouping oxidizable by hypoiodite and believed to be a lignin component in many cases remained behind. Their conclusion was that if a major fraction of the organic matter is predominantly lignin-derived, the processes of decomposition reduce its ability to undergo reactions as normally bring about solution.

Since good yields of recognizable products have been obtained by alkaline nitrobenzene oxidation and high-pressure catalytic hydrogenation of plant lignin, Gottlieb and Hendricks [160] applied these two methods to soil organic matter in the hope that characteristic products would be obtained enabling the positive identification of lignin-like material. Although they could not isolate such products they were able to draw certain conclusions from their results. These conclusions may be summarized as follows:

1. The material derived from plant lignin in the soil is drastically altered in the kind and position of the peripheral groupings on the aromatic rings.
2. If lignin-like materials are present in soil organic matter, a large percentage of the original hydroxyl groups are absent and carboxyl groups have appeared.
3. Soil preparations bear a striking resemblance to alkali lignin in their behaviour towards hydrogenation.

Further evidence that plant lignins are altered in the processes leading to the formation of soil organic matter has been provided by studies on the biological decomposition of plant materials outside the soil. Such investigations have shown that although the lignins of plant materials are relatively resistant to attack by micro-organisms and tend to accumulate, they do undergo definite changes as decomposition proceeds. These changes apparently involve oxidation and the introduction of carboxyl groups and are reflected by an increase in exchange capacity and nitrogen content and by a decrease in the number of methoxyl groups [158, 161].

These results are in harmony with the findings of Gottlieb and Hendricks and Norman and Moody and with the results obtained by Gillam, Forsyth, and other workers in studies on the humic complexes of soil. It may be concluded, therefore, that if a major fraction of soil organic matter is lignin-derived, the amount in the form of unaltered lignin is not appreciable. The indications are that plant lignins entering the soil undergo changes which lead, for example, to the introduction of carboxyl groups with consequent increase in alkali solubility and exchange capacity and to the loss of methoxyl and hydroxyl groups, and that as a result of these changes they fail to give some of the chemical reactions that are regarded as characteristic of plant lignins.

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(*Received 25 June 1953*)

THE DETERMINATION OF THE STABILITY OF SOIL CRUMBS

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I. Limitations of Existing Methods

The stability of soil crumbs has frequently been characterized by determining their resistance to breakdown in water. This may be done in two ways. In the first, originated by Tiulin (1928), the dry crumbs are placed on top of a bank of sieves, wetted, and the size distribution of the wetted crumbs determined after agitating the sieves under water. Modifications designed to prevent further breakdown when separating the wetted crumbs have been devised by Childs (1940) and by Zeller (1951). The second way, due to Middleton (1930), instead of reducing mechanical breakdown after wetting to a minimum, measures the degree of dispersion produced by a given amount of mechanical action. This is usually done by shaking the crumbs in water in an end-over-end shaker for a fixed time.

During the last 20 years, many attempts have been made to correlate the water stability of crumbs determined by either of the above methods with the amounts of organic matter and clay present in the crumbs and the cropping history of the fields from which the crumbs were taken. The results are very variable; but there appear to be two distinct situations according to whether the crumbs come from arable soil or grassland. For grassland, a good correlation has been found between organic carbon and water stability by Ackerman and Myers (1943), Low (1950), and by Russian workers under Williams. For other crops, several authors, Stauffer *et al.* (1940), Rogers (1939), Retzer and Russell (1941), and Ackerman and Myers (1943), have shown that the effect of the crop outweighs any effect of organic matter on aggregate stability, and lucerne appears to be particularly effective in promoting water stability. Regarding clay content, there seems to be general agreement that it is a major factor in determining crumb stability (Puri *et al.* 1939; Hénin, 1938; and Sideri, 1938).

The following paper is an attempt to elucidate the various factors influencing the results obtained, and to consider the relevance of the method as a whole to the problem of soil structure in the British Isles.

Causes of Crumb Breakdown

The factors governing the breakdown of dry aggregates when wetted by a liquid can be broadly grouped under two main headings: slaking of the aggregates and dispersion of the clay in the aggregates. For simplicity it has been assumed that the crumbs are effectively calcium-saturated, as is normal in the British Isles. Under these conditions, breakdown due to swelling of the clay has been shown to be unimportant (Emerson and Grundy, 1953).

In the following diagram the various factors are subdivided into those

SLAKING
(Disruption by entrapped air)
Volume of air entrapped
Mechanical strength of crumbs
(cohesion)
Rate of wetting
Pore geometry of crumb
Initial moisture content of crumb
Tendency for clay to disperse
Amount of clay
Method of wetting crumb
Surface tension of wetting liquid
Contact angle liquid-soil
DISPERSION
Clay minerals present
Electrolyte content of wetting liquid
Dielectric constant of wetting liquid
Bonding of clay crystals by organic or inorganic compounds

fixed by the crumbs themselves, shown in italics, and those which depend on the particular method used to estimate the stability of the crumbs. The importance of the latter will be considered, in particular the rate of wetting and the electrolyte content of the wetting liquid.

Rate of Wetting

The importance of the rate of wetting on cohesion is shown in Fig. 1, which is for 2–5 mm. air-dry crumbs from an old arable field (Barnfield, Rothamsted) and from an adjoining permanent pasture (Emerson and

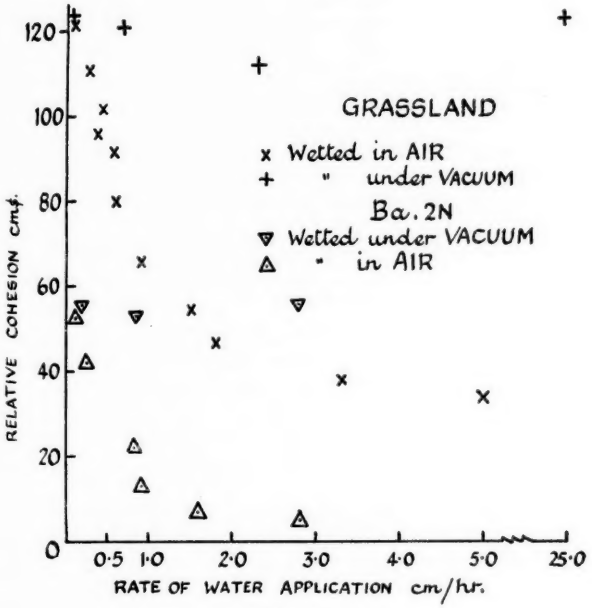

FIG. 1.

Grundy, 1953). The relative cohesion of the crumbs was measured by the height from which 40 drops of water would cause 0·15 g. out of approximately 1 g. of the wet crumbs to pass through a 1·2-mm. aperture gauze. The cohesion of the crumbs falls very rapidly as the rate of wetting increases. When comparing the stability of crumbs, therefore, small differences in their rates of wetting may give erratic results.

In the two techniques outlined in the introduction the crumbs are usually wetted by immersion, so that the rate of wetting is indeterminate. Some idea of their behaviour, however, may be inferred from their rates of water absorption at very low suctions. For these measurements crumbs from the 0·4-in. layers of the adjacent plots 2 N and 4 N on Barnfield, the permanent mangold field, and from nearby permanent grassland were used. Barnfield 2 N and 4 N have both received a

complete fertilizer annually, but 2 N has had in addition 14 tons/acre of f.y.m. As will be seen from Table 1, the crumbs from these locations differ in their organic matter content but are otherwise similar.

TABLE 1

Mechanical Analysis of Soils Used

	Grassland %	*Barnfield 2 N* %	*Barnfield 4 N* %
Coarse sand .	6	6	6
Fine sand .	43	39	39
Silt . . .	26	24	24
Clay . .	18	18	18
Carbonate .	1·0	0·5	0·5
Organic carbon .	5·0	3·1	0·8

The apparatus used consisted of a coarse sintered-glass Büchner funnel, 6·5 cm. in diameter, connected by rubber tubing to a horizontal glass tube graduated to 0·1 c.c. The height of the tube was adjusted so

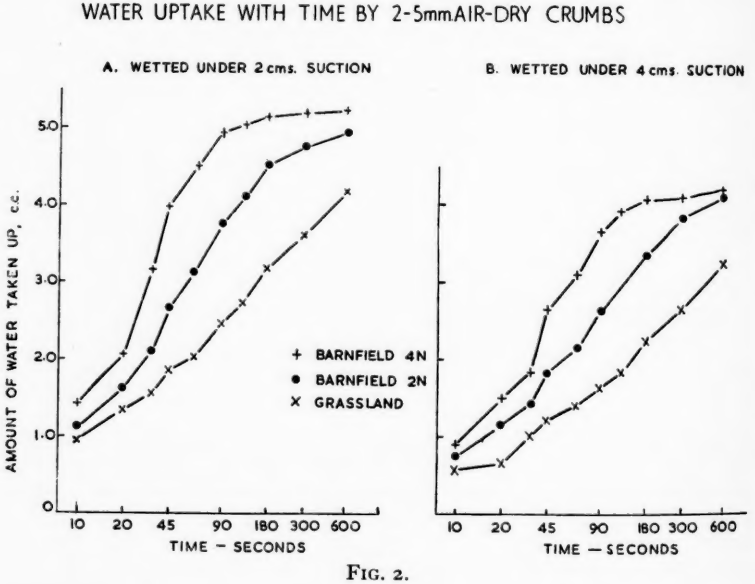

FIG. 2.

that the vertical distance between it and the top of the sinter was equal to the suction required, namely 0·5 cm. or 2·5 cm. The apparatus was filled with distilled water. Ten grammes of 2–5 mm. air-dry crumbs were then tipped quickly into the funnel and the rate of water uptake with time determined.

The results based on the mean of three samples are shown in Fig. 2.

There are marked differences between the three soils, the grassland crumbs wetting more slowly than the Barnfield 2 N crumbs which again wet more slowly than those from plot 4 N. The effect is particularly marked at the lower suction, the grassland crumbs taking up water at about half the rate of the 4 N crumbs. Referring to Fig. 1, since at the same rate of wetting the cohesion of the grassland crumbs is higher than that of 2 N, the slower rate of wetting, shown above, will accentuate the difference between the arable and grassland soils.

It appears that organic matter after air-drying is not easily re-wetted or, in other words, that the contact angle of water advancing into a soil containing much organic matter is appreciable.

This has been shown indirectly in another way by Myers (1941) and Hénin (1948), who replaced the air in the crumbs with a liquid non-miscible with water. On wetting with water, the breakdown due to entrapped liquid should be much higher than the breakdown caused by similarly trapped air, since the liquid is incompressible. Hénin found that the stability of soils low in organic matter was much decreased whereas it had little effect on soils with a high content of organic matter, presumably because these wet so much more slowly whether air or an organic liquid is present. The large contact angle of air-dry organic soils is undoubtedly one important reason why a correlation has been found between organic matter content and water stability as judged by the methods hitherto employed.

Very high contact angles may also be produced artificially by the products of bacterial and fungal action. Several experimenters (including Swaby, 1950) have shown that a nutrient solution added to a soil will cause sufficient bacterial and fungal growth to make the crumbs practically waterproof. This again will give a high figure for water stability since the crumbs wet only very slowly.

Electrolyte Content of Wetting Liquid

The next factor to be investigated was the effect of using distilled water as the wetting agent. As a first step, the concentrations of calcium chloride required to flocculate surface soils of various Rothamsted fields were determined. This was done by suspending 5-g. samples of untreated soil in a series of test-tubes containing 50 c.c. of a range of calcium chloride concentrations. The criterion of flocculation was a clear supernatant liquid after standing overnight. The equilibrium concentration of $CaCl_2$ in each tube was determined by measuring the resistance of the supernatant liquid in a calibrated cell. The soils examined were Hoosfield 4 A, Broadbalk, Barnfield 8 O, Barnfield 2 N, and Sawyers I. The first three were flocculated at a concentration of 2×10^{-3} M., but deflocculated when the concentration was reduced to 1×10^{-3} M. For the last two the concentration of $CaCl_2$ had to be increased to 3×10^{-3} M. for flocculation. A sample of Gault clay behaved in the same way as the first three soils. This suggested that percolating crumbs from the above soils with a solution of calcium chloride less than 1×10^{-3} M. would cause breakdown due to dispersion of the clay, and experiments were made to test this.

Twenty grammes of natural 1–2 mm. air-dry crumbs from samples of the surface soil of Barnfield 2 N, Barnfield 4 N, and Sawyers I (a soil of similar mechanical composition, but containing no free $CaCO_3$) were wetted with distilled water on a coarse sintered glass Büchner funnel under a suction of 9 cm. of water. The crumbs were then flooded, covered with a No. 4 filter-paper, and a 500-c.c. flask containing distilled water was inverted in the clear liquid above the crumbs. Percolation was then started and the crumbs and leachate watched for evidence of dispersion. No breakdown of crumbs was observed and no dispersed clay appeared in the leachate. The first leachate from Barnfield 2 N was slightly yellow, due to organic matter. It was noted, however, that if the flask was not inverted carefully the consequent disturbance to the crumbs caused some dispersion. There appears to be an energy barrier to be overcome before the clay will disperse.

An opportunity to test this metastability of calcium-saturated crumbs in the field was afforded by the three Rothamsted drain-gauges. These consist of bare, isolated blocks of natural soil, 20 in., 40 in. and 60 in. deep respectively and one-thousandth of an acre in area. A very heavy dressing of lime was given just before the gauges were made 80 years ago. Samples of the drainage water were taken on 1 and 2 May 1953. There had been no rain for 3 weeks, so the drainage in the first day at least should have been in equilibrium with the soil. The samples were taken in stoppered Winchesters which were filled completely so as to help prevent atmospheric CO_2 from affecting the calcium-ion concentration. The pH of the sample was measured immediately. The concentration of calcium was determined by a flame photometer and the bicarbonate-ion concentration by titration. The pH readings on the first day were unreliable and have been omitted. The bicarbonate-ion concentration was not determined on the second day, as it was obvious from the first day's readings that all the calcium in the solution was present as bicarbonate. The other results are given in Table 2, the concentrations quoted being molar.

TABLE 2

	1 May		*2 May*	
Gauge	Ca	HCO_3	Ca	pH
20 in.	$6{\cdot}6\times10^{-4}$	$1{\cdot}25\times10^{-3}$	$6{\cdot}1\times10^{-4}$	7·90
40 in.	$6{\cdot}6\times10^{-4}$	$1{\cdot}25\times10^{-3}$	$6{\cdot}0\times10^{-4}$	7·87
60 in.	$7{\cdot}1\times10^{-4}$	$1{\cdot}42\times10^{-3}$	$6{\cdot}6\times10^{-4}$	7·85

Using the published values of the equilibrium constants the above results closely approximate to a calcium bicarbonate solution in equilibrium with atmospheric CO_2. This implies that free $CaCO_3$ is still present and, as might be expected, there is now little bacteriological activity.

It will be seen that the calcium-ion concentration is about half that required for flocculation and yet the leachate has always been clear. In periods of heavy rainfall presumably the concentration will fall below that given above.

It is of interest to calculate what the pH of a soil containing free calcium carbonate has to be so that the equilibrium calcium-ion concentration will be sufficient to maintain the clay flocculated. For a CO_2 concentration of 0·1 per cent., an average figure for soils, the calcium-ion concentration in the soil solution will be greater than 2×10^{-3} M., provided the pH is less than 8·0. In practice, therefore, it would be expected the drainage water from soil containing free calcium carbonate should be free from dispersed clay. This is of particular importance for mole drainage where silting up is a cause of failure. It is known that clay formations containing considerable quantities of free calcium carbonate, such as Gault, are particularly suitable for mole draining (Nicholson, 1942).

On the other hand, it is now apparent that if distilled water in the Tiulin test is used very different results will be obtained according to the speed of sieving. If the speed is slightly too high, considerable mechanical breakdown may occur by the crumbs being jerked on and off the sieves. It also explains why there is always a decrease in the weight of crumbs on the sieves with time, which is particularly marked with crumbs of low stability. Russell and Feng (1947) have even tried to express this decrease mathematically and extrapolate back to zero time to obtain their stability figures.

The second general test (Middleton), using end-over-end shaking in distilled water, seems even less satisfactory than the wet sieving technique, for if shaken sufficiently all the clay would go into suspension. This was found by Nijhawan and Olmstead (1947), who could reduce the amount of aggregation to any desired level by end-over-end shaking.

The susceptibility of the crumbs to mechanical dispersion when the calcium-ion concentration falls below 2×10^{-3} M. is of practical importance. It is generally recognized that applying lime to heavy clay soils improves their structure, but water stability tests have failed to pick up any beneficial effect (Rost and Rowles, 1940; Baver, 1936). This is because the soil sample is immersed in about 100 times its volume of distilled water, so that, in effect, it is the stability in distilled water which is measured. In the field, liming may appreciably affect the concentration of calcium in the soil solution. In a drainage experiment on a non-calcareous clay soil Childs (1943) observed that the amount of suspended material in the drainage water from limed plots was only one-third that from unlimed plots.

Discussion

Two processes have to be distinguished in water stability tests: the slaking of crumbs on wetting due to entrapped air, and the subsequent disintegration of the wetted crumbs by mechanical action. Since these tests are used to characterize soil structure in the field, it is necessary to assess the relative importance of these two processes. In the British Isles the intensity of rainfall seldom exceeds 0·2 cm. per hour. On referring to Fig. 1 it will be seen that the cohesion of dry crumbs wetted at this rate in air is almost the same as for those wetted under vacuum, so that breakdown due to entrapped air is, therefore, unimportant. The

major cause of crumb breakdown in the field must be the mechanical action of raindrops causing dispersion of the clay. This leads to the familiar bleached appearance of fields after a rainstorm produced by exposed sand grains on the surface. In areas with high rainfall, however, both slaking and mechanical action will be important. Yoder (1936) has, in fact, used the wet-sieving technique to assess the erodability of soils.

The degree of breakdown caused by falling rain will depend on the cohesive strength of the crumbs when wet. The suction of the wet surface crumbs should, therefore, be maintained as high as possible while rain is falling. This may be an important way in which drainage improves the structure of clay soils.

One factor which has not been mentioned hitherto is the dielectric constant of the wetting liquid. Since the maximum thickness of a liquid film on the negatively charged surface of clay crystals varies as the square root of the dielectric constant (Schofield, 1946), the lower the dielectric constant the closer together the clay crystals will remain and hence the higher the cohesion of the crumbs. This may account for the 'anomalously' high cohesion of crumbs wetted with ethyl alcohol (Myers, 1941; Hénin, 1948).

Summary

The breakdown of soil crumbs in conventional water stability tests is a result of the combined effects of slaking and dispersion. The various factors influencing the effectiveness of these two processes have been divided into those determined by properties of the crumbs themselves and those dependent on the technique used. Two of the latter have been considered in detail, namely the method of wetting and the electrolyte content of the wetting liquid. It has been concluded from a comparison of the rates of water uptake by crumbs containing various amounts of organic matter that water has an appreciable advancing contact angle with air-dry organic matter. This may have been the main cause of the correlation found by previous workers between water stability and organic matter for soils high in organic matter.

It has been shown that calcium-saturated crumbs are metastable in distilled water but will disperse if mechanically disturbed. In conventional water-stability tests some continuous mechanical disturbance of the crumbs is inevitable so that the apparent stability of the crumb always decreases with time. Also in these tests the crumbs are always immersed in a large excess of distilled water so that the results obtained are independent of the calcium-ion concentration of the soil solution. In the field any increase in this concentration will make the crumbs more resistant to mechanical action.

II. A New Method for Moist Crumbs

It has been shown in Part I that results obtained by existing methods are difficult to assess because the rate of wetting is not controlled and also because distilled water is used as the wetting agent. As slaking appears

to be unimportant under English conditions, in the method outlined below any breakdown due to this factor is eliminated by wetting the crumbs very slowly under suction. The problem now is to measure the resistance of the wetted crumbs to breakdown by dispersion.

It is known that if montmorillonite is saturated with sodium, as the concentration of sodium salt is reduced the montmorillonite sheets gradually expand, until at a certain concentration the attractive forces are no longer sufficient to keep the plates together and the clay spontaneously disperses (Hofmann and Bilke, 1936). Similarly for illite and kaolinite the thickness of the water-films on the negatively charged faces of the crystals gradually increases as the concentration of electrolyte is reduced. Na-illite and Na-kaolinite might be expected to disperse spontaneously at about the same concentration as montmorillonite since the thickness of the water-films, at least at low concentrations of sodium salt, is almost independent of the surface density of charge provided this is high enough (Schofield, 1946). It was thought that if soil crumbs were sodium saturated, differences in the attractive forces holding the crumbs together would be reflected by the concentration of electrolyte at which they spontaneously disperse.

Since most of the salt concentrations quoted in this paper are below normal, it has been found convenient to express all concentrations in terms of milli-normality (mN).

Soils Used

In addition to the grassland and Barnfield 2 N soils described in Part I, soil from Barnfield 8 O and Willaluka subsoil were used. The mechanical analyses of the last two are:

TABLE 3

Mechanical Analysis of Soils used

	Barnfield 8 O %	*Willaluka subsoil* %
Coarse sand . .	6	2
Fine sand . .	38	38
Silt . . .	21	3
Clay . . .	29	57
Carbonate . .	0·5	0·02
Organic carbon .	0·7	0·8

Barnfield 8 O has had no fertilizer, artificial or organic, since 1876. The average yields of mangolds for 2 N and 8 O are 27 and 3 tons/acre respectively.

The clay fraction of the Barnfield soil is mainly illite with some kaolinite. The Willaluka subsoil is an Australian soil, whose clay fraction is almost pure fine illite.

Experimental Procedure

The apparatus used is shown in Fig. 3. It consists of a Büchner-type funnel, 6·5 cm. in diameter, with a sintered glass base having an average pore size of 40–50 microns, connected by rubber tubing to a tap and then to a short glass siphon.

The system had first to be filled with 500 mN. NaCl. Having removed the siphon tube, the funnel was inverted in a beaker containing the

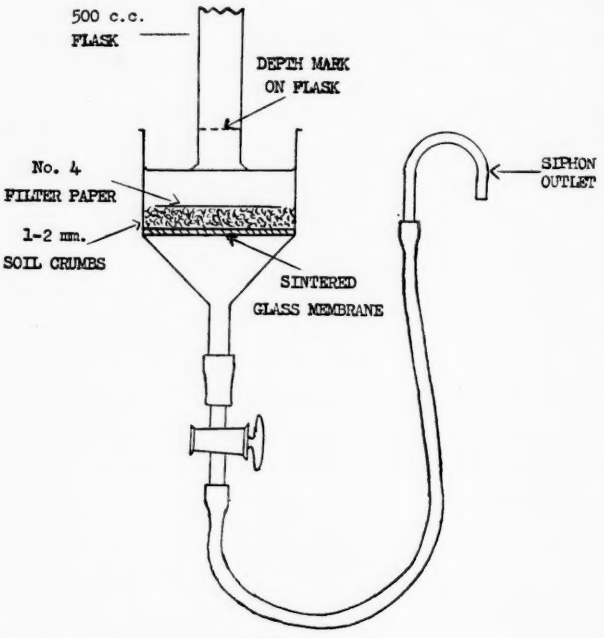

FIG. 3.

sodium chloride solution. This solution was then sucked in until the apparatus was full and the tap was then shut. Next the funnel was removed from the beaker and set up with the end of the rubber outlet tube 12 cm. below the sintered glass base. Twenty grammes of 1–2 mm. air-dry crumbs were then poured in stages into the funnel, keeping the depth of crumbs as uniform as possible. At the same time as the crumbs were wetted by the solution, more solution was added by a pipette to the side tube to maintain the suction on the crumbs at 12 cm. As soon as the rate of uptake of solution became negligible the side tube was raised, so reducing the suction on the sample, and more solution added until the uptake again became negligible. Finally, by raising the tube above the base of the crumbs and slowly running solution in, the crumbs were immersed with about 3 cm. of clear liquid above them. A No. 4 filter-

paper was floated down on to the surface of the crumbs so as to minimize disturbance to them when the flask containing the percolating solution was changed. The flask, usually of 500-c.c. capacity, was inverted in the solution to a fixed depth below the top of the funnel so as to maintain a constant head.

The crumbs were percolated slowly with 1 litre of 500 mN. NaCl over a period of 2 days, the rate of flow being regulated by adjusting the tap. Near the end of that time the height of the siphon tube was adjusted to give a rate of flow of about 5×10^{-1} c.c./sec. This height was kept constant throughout the experiment so that the rate of flow measured was always proportional to the permeability. The flask was then removed, the tap shut, and most of the excess solution above the filter-paper carefully pipetted off. Sufficient of the weaker solution to be used next, say 50 mN. NaCl, was then slowly pipetted into the funnel to restore the solution to its original level. The flask, now filled with the more dilute solution, was then inverted into the funnel to the same depth as before, and the tap opened. The permeability was measured immediately afterwards and, subsequently, at intervals of time determined by the speed at which the permeability was changing. The leachates between the permeability determinations were collected. The concentration of sodium chloride in them was measured by their resistance in a calibrated cell, using a 1,000 cycles/sec. oscillator and a Wheatstone bridge. The turbidity of the leachates was estimated by the reading of a photo-electric cell using a green filter. Percolation with the solution was usually continued until the concentration of the leachate became equal to that in the flask.

Results

The change in the permeability of the crumbs and the change in the concentration and turbidity of the percolating solution with time are shown in Figs. 4 and 5. The scale interval of time is 1 hour except where a wavy line is shown joining two points which denotes the sample was left overnight. The arrows indicate where the flask was refilled. The permeability plotted is not the actual permeability of the crumb bed but is the permeability as measured, i.e., of the crumbs and the sintered glass disk. This has the advantages both of convenience and of compressing the scale, in that initially the crumbs themselves offer a negligible resistance to flow. However, as soon as the crumbs begin to swell appreciably it is the crumb bed itself which controls the permeability.

Referring to Fig. 4, having brought the grassland crumbs into equilibrium with 500 mN. NaCl, the solution was replaced by 20 mN. NaCl. The permeability fell slightly with time as the concentration was reduced and a certain amount of clay was dispersed, as shown by the leachates being slightly turbid. The concentration of the leachate having fallen to 22 mN., the percolating solution was changed to 5 mN. The permeability steadily decreased for 2 hours and then flow was stopped overnight. Next morning the flask was refilled with the same strength of solution and the permeability determined immediately afterwards.

Although the concentration of the leachate was about the same as the previous evening, the permeability had fallen by 35 per cent. and the leachate was very turbid. Part of this could be explained by crumb breakdown caused by the mechanical disturbance of changing flasks in spite of the care taken, but most of it was probably due to slow swelling

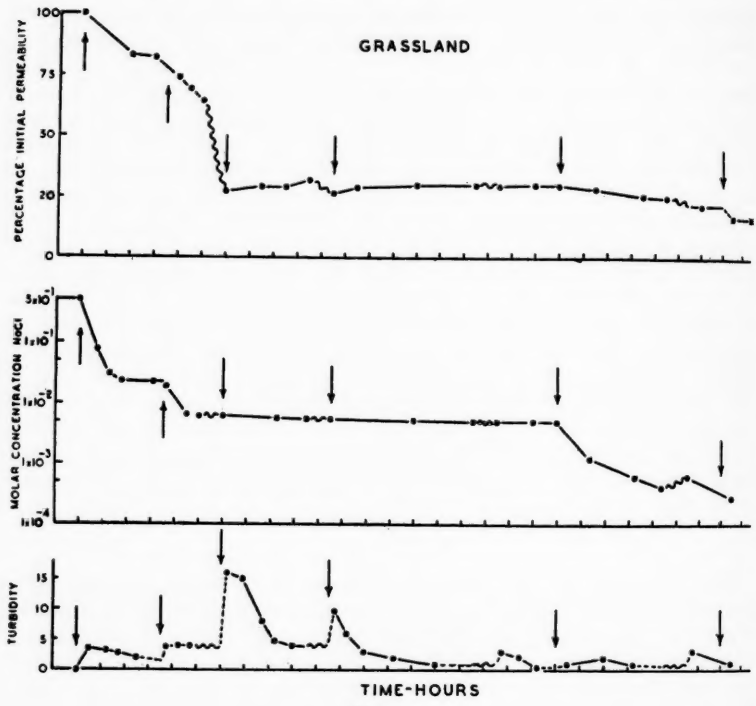

FIG. 4.

of the clay. Continuing with the same solution all day the permeability rose slightly as the dispersed clay was flushed from between the crumbs. After leaving shut off overnight, 5 mN. NaCl was again percolated through. The permeability was reduced slightly compared with the previous night and the leachate was again fairly turbid. After leaving the solution flowing all day and night, the permeability had not changed appreciably by the morning although the turbidity of the leachate increased slightly. The concentration of the percolating solution was reduced subsequently to 0·3 mN., causing only a slight reduction in permeability, and only a very small amount of dispersed clay appeared in the leachate.

Now referring to Fig. 3 and the Barnfield 2 N curve, lowering the concentration to 22 mN. caused a slightly greater percentage decrease in permeability compared with the grassland crumbs (36 per cent. instead

of 18 per cent.) and slightly more dispersed clay appeared in the leachate. However, on refilling the flask with 5 mN. the filtrate became extremely turbid, the crumbs began to break up, and the permeability dropped in 3 hours to 5 per cent. of its initial value. The flask was then refilled with 5 mN. NaCl and left running overnight. By the morning the permeability was practically zero and there was just an amorphous mass of soil.

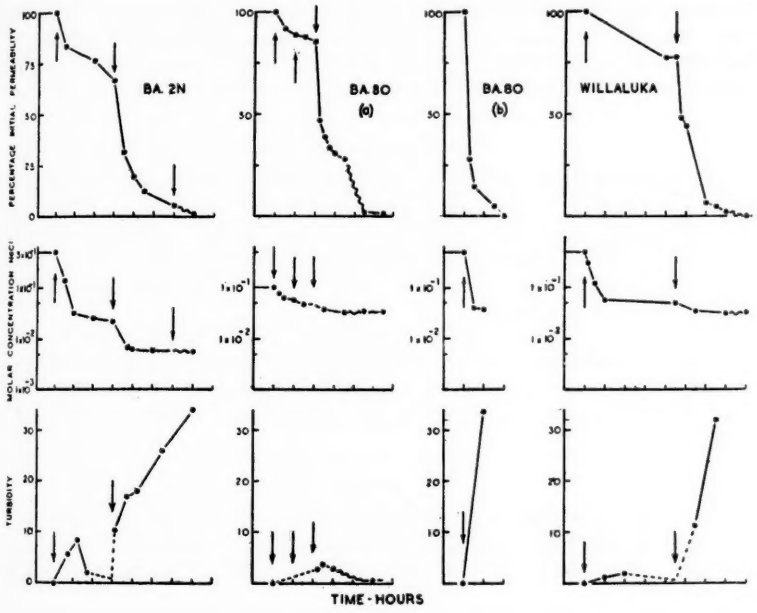

FIG. 5.

In the case of Barnfield 8 O (*b*), on changing the concentration of the percolating solution from 500 mN. to 25 mN. the permeability fell very sharply, the leachate becoming increasingly turbid. At the end of 2 hours the crumbs were completely dispersed and impermeable. There was insufficient filtrate to measure the concentration after 1 hour, but presumably the concentration after 2 hours was only slightly lower than that at 1 hour, namely 38 mN.

In 8 O (*c*) the experiment was repeated, but this time the concentration was reduced much more gradually. After leaching for 12 hours with 500 NaCl the sample was percolated overnight with 100 mN., which gave a completely clear leachate. Reducing the concentration successively to 50 mN. and 33 mN. decreased the permeability by 15 per cent. with a negligible amount of dispersed clay in the leachate. On changing to 25 mN. NaCl, however, the permeability decreased 55 per cent. in 1½ hours. By next morning, after standing all night with the tap shut, the crumbs were barely distinguishable and formed an almost impermeable

bed. The concentration of the leachate had not changed since the previous evening, namely 34 mN. It will be noted that in contrast to the previous experiment the leachate remained practically clear; that is, the clay itself did not disperse.

Finally, for the Willaluka subsoil, changing the concentration to 50 mN. reduced the permeability about 20 per cent., which is slightly more than for the Ba 8 O and presumably due to the greater clay content. On lowering the concentration to 33 mN. the permeability decreased very sharply and large amounts of dispersed clay appeared in the leachate. After standing overnight the crumbs were completely dispersed and impermeable and in equilibrium with a concentration of 34 mN.

Flocculation Behaviour

The concentrations of NaCl required to flocculate sodium-saturated suspensions of the soil were determined by repeated dilution and measuring the resistance of the supernatant liquid. The criterion for flocculation was a clear supernatant liquid after standing for 24 hours. The soil was prepared by leaching 2–5 mm. crumbs with 500 mN. and then with 50 mN. NaCl.

The effect of adding small quantities of dilute alkali or acid on the flocculation concentration was determined for sodium illite derived from the Willaluka subsoil and for sodium saturated Wyoming bentonite. The effect of sodium alginate on the flocculation of the illite was also observed.

Results

The concentrations of sodium chloride required to flocculate suspensions of Barnfield 2 N soil and grassland soil were found to be about the same, namely 250 mN. That for the Barnfield 8 O was lower, namely 40 mN.

The illite as dispersed from the Willaluka crumbs flocculated at 25 mN. NaCl. By repeated decantation and each time adding about 0·1 c.c. of 50 mN. HCl the flocculation concentration was reduced to below 0·4 mN. NaCl. Adding a small quantity of 50 mN. NaOH increased the flocculation concentration to 70 mN. NaCl. When a small quantity of 1 per cent. neutral solution of sodium alginate was added to Na illite dispersed in distilled water, the concentration of NaCl required for flocculation rose to between 250 and 300 mN.

The addition of similar small quantities of dilute alkali and acid had much less effect on the flocculation behaviour of Wyoming bentonite. Alkali had a negligible effect, the flocculating concentration remaining at about 20 mN. NaCl, but the addition of acid reduced the concentration required for flocculation to 6 mN. NaCl.

Discussion

By wetting the air-dry crumbs very slowly under suction, differences in breakdown due to slaking have been eliminated. The method has given marked differences in behaviour between the various soils.

Considering the results for the Willaluka subsoil first, there is a definite concentration of NaCl at which the crumbs disperse, namely 34 mN. This may be called the critical concentration for this soil. The Barnfield 8 O crumbs in experiment (*b*) behaved almost identically, dispersing completely at about the same concentration. In experiment (*a*), where the concentration of the percolating solution was reduced much more slowly, although the crumbs broke up and became almost impermeable at the same concentration as in experiment (*b*) the clay itself did not disperse. From the point of view of structure this difference is of no importance; the crumbs do in fact disintegrate at this concentration. The critical concentration for the Barnfield 2 N soil is much lower, 5 mN., indicating the much higher cohesive strength of these crumbs compared with the Barnfield 8 O. The grassland crumbs, because they are able to withstand distilled water, show still greater cohesion. It must be emphasized that every care must be taken to avoid mechanically disturbing the crumbs, since below 200 mN. the crumbs would disperse if shaken into suspension and are therefore in an unstable state of equilibrium. There is also a time-lag in the response to changing the concentration of the percolating solution, especially near the critical concentration. However, provided the concentration in the flask is not changed until the permeability becomes constant, no difficulty should arise.

A direct outcome of this work is its application to the reclamation of flooded or alkaline soils. If these fields are in grass it may be possible to maintain the structure of the surface soil without gypsum treatment, since distilled water may be percolated through without serious structural decline. This is borne out by experience in Holland. Further, it underlines the importance of organic matter content as well as exchangeable sodium percentage in the treatment of alkali soils. This has been emphasized also by Antipov Karataev (1943).

An important factor which has not been controlled in these experiments is the pH. Schofield and Samson (1953) have shown that kaolinite crystals in addition to their permanent negative isomorphous replacement charge have edge faces which are positively charged at low pH. This positive charge is reduced as the pH is increased, disappearing completely at about pH 9·2 in N/200 KCl. From the similarity in crystal structure, the same kind of behaviour would be expected from the edge faces of illite and montmorillonite. This would explain the much lower flocculation concentration for illite where the pH was reduced by the addition of dilute HCl, since with positive charges on the edge, edge-to-face flocculation may occur. Similarly, by adding alkali and thus raising the pH and eliminating much of the positive charge, the flocculation concentration was increased to 60 mN. The same kind of effect was observed for Wyoming bentonite, although it was reduced in magnitude because of the thinness of the plates.

Sodium-saturated illite dispersed in water, after adding sodium alginate, required between 250 and 300 mN. NaCl for flocculation. This makes it about the same as that found for suspensions of soil from Barnfield 2 N and the grassland, namely 250 mN. Further, Samson

(unpublished 1953) has shown that sodium-saturated kaolinite, which normally flocculates in distilled water, requires a concentration of 100 mN. NaCl if a small amount of sodium alginate is added. Van Olphen (1951) found that a French bentonite treated with the sodium salt of quebracho (a polyphenolic compound) required 280 mN. NaCl for complete flocculation and Wyoming bentonite 300 mN. NaCl. The three clay minerals, therefore, when sodium-saturated flocculate at about the same concentration of NaCl when certain large organic molecules are present in spite of the differences in thickness and charge density of the individual clay platelets.

However, Schofield (1946) has shown that the distance apart of and repulsion force between two negatively charged plates in a sodium chloride solution depends only on the external salt concentration and is independent of charge density provided this is greater than about 5×10^{-8} m.e./cm.^{2} Further, the Van der Waal's attractive forces between two plates are functions mainly of their distance apart and only to a small extent of the thickness of the plates (Verwey and Overbeek, p. 101). In the case, therefore, where Van der Waal's forces are the only attractive forces, sodium-saturated suspensions of bentonite, illite, and kaolinite might be expected to flocculate at about the same concentration of NaCl.

The concentration of NaCl required to flocculate suspensions of Barnfield 8 O and the Willaluka subsoil is much lower, namely 40 mN. and 30 mN., and is about the same as the critical concentration for the crumbs. In the virtual absence of organic matter, therefore, flocculation in a sodium-saturated system appears to be a reversible state of equilibrium, i.e., whether approached by reducing the concentration of flocculated suspensions or increasing the concentration of dispersed suspensions. The lower salt concentration at which flocculation occurs, compared with pure clay suspensions with small amounts of long chain compounds added, may reflect additional attractive forces due to positive edges.

Compared with Barnfield 8 O, the grassland crumbs not only show very great resistance to dispersion, but also conversely if shaken into suspension require a much higher concentration of NaCl for flocculation. Further, the flocculation concentration is comparable with that found for the sodium-saturated clay minerals with a small quantity of certain large organic molecules added. In suspensions, therefore, it is possible that organic molecules in the grassland crumbs neutralize the positive edges of the clay crystals. On the other hand, in the crumbs where the clay is flocculated initially it may be possible for the same organic molecules to bridge several clay crystals, thus providing an additional attractive force against dispersion.

If the fraction of the soil organic matter responsible for crumb stability is held by the positive edges of the clay plates, it should be possible to leach it out by raising the pH of the soil to a point where the edges of the clay are neutral or, better still, negatively charged. It is interesting to note that Forsyth (1951), who examined the fraction released by leaching with 200 mN. NaOH, i.e., at about pH 12, was able to isolate a pure polysaccharide from a wide variety of soils.

Summary

A new method for characterizing the stability of moist soil crumbs which avoids breakdown due to slaking has been described. The crumbs are slowly wetted under suction with a strong sodium chloride solution and then leached with this solution until sodium saturated. The crumbs are then percolated with increasingly dilute concentrations of sodium chloride and the changes with time of the permeability of the crumbs and the concentration of salt in the leachate are measured. The concentration at which the crumbs completely break up and their permeability falls effectively to zero is called their critical concentration. The critical concentration for two plots from Barnfield 8 O and 2 N (the first having received no fertilizer or organic manure, and the second 14 tons/acre f.y.m. and balanced artificial manuring annually for 80 years), and the adjoining permanent grass, with the same mineralogical constitution, were found to be 34, 5, and less than 0·3 mN. NaCl respectively, indicating the very marked differences in the cohesive strength of the crumbs.

By observing the effect of adding dilute alkali and acid on the concentration of electrolyte required to flocculate sodium-saturated suspensions of pure illite and montmorillonite, it was inferred that positive charges were present on the edges of the platelets, as shown already for kaolinite by Schofield and Samson (1953). The flocculation concentration for illite with sodium alginate added was found to be between 250 and 300 mN. NaCl. This agrees well with determinations of the flocculation concentration for montmorillonite and kaolinite found by other workers using certain large organic molecules.

The flocculation concentrations of sodium-saturated suspensions of the Barnfield 8 O and Willaluka soils were found to be equal, namely 30 mN. NaCl. This is the same as the critical concentration for crumbs of these soils. In the virtual absence of organic matter, therefore, flocculation appears to be a reversible state of equilibrium. The concentration of NaCl required to flocculate sodium-saturated suspensions of the grassland soil was 200 mN., which is about the same as that for suspensions of pure clay minerals in the presence of long chain molecules.

It is suggested that the additional cohesive force of grassland crumbs is due to linkage of the positive edges of clay crystals by long chain organic molecules. The reduced attractive forces in suspensions of the grassland soil compared with Barnfield 8 O soil may be due to the absence of positive edge-negative attraction as a result of each molecule being linked to the edge of one clay crystal only.

Acknowledgements

The author wishes to thank Mr. W. C. Game and Mr. A. W. Taylor for their help in obtaining the drain-gauge results, and to acknowledge his debt to the previous work carried out by Dr. Quirk and Dr. Samson in the Physics Department under the direction of Dr. Schofield.

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(*Received 27 August 1953*)

INVESTIGATIONS INTO THE MECHANISM OF SOIL ADHESION

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Synopsis

Investigations into the mechanism of the adhesion between soil and foreign surfaces in normal loading tests are described. The adhesion is found to be entirely due to the water film between the joined surfaces, and its magnitude is approximately equal to the moisture tension in this film multiplied by its area. The effects of the soil, the foreign material, and the testing technique on the tension in the moisture film are discussed.

Introduction

THE phenomenon of soil 'stickiness' has always occupied a prominent place among the investigations of soil physicists because farmers find it one of the soil's most troublesome physical properties. An excessively sticky soil makes cultivations difficult and prevents the harvesting of root crops in a clean condition. Much of the present knowledge of soil stickiness centres around the concept of 'sticky point', which may be defined as the minimum soil moisture content at which the *cohesion* of a soil is less than its *adhesion* to a foreign object. A soil at this moisture content is just wet enough to cling to a spatula drawn across its surface. It is found in practice that the sticky point of the soil is not as indeterminate as might be expected from the definition, and independent workers generally achieve remarkably close agreement as to its value for a particular soil. Atterberg (1911) was one of the first workers on soil stickiness, and the concept of 'Klebegrenze' which he introduced appears to be almost identical with the sticky point of later workers such as Keen and Coutts (1928) and Hardy (1928). The determination of the sticky point of soils after they had been treated in various ways has provided useful information as to which soil constituents hinder and which help the cultivation of soil with high moisture contents (Marchand, 1930; Prescott and Poole, 1934). Though these determinations have considerable empirical value, they are only of limited help in elucidating the real nature of soil stickiness. The investigations described in this paper concern one aspect of soil stickiness only, the *adhesion* between soil and a solid surface. All the experiments were carried out under conditions such that failure took place at the foreign surface/soil interface and not within the soil itself.

Theory

It may be supposed that the adhesion between soil and a foreign object is due partly to direct attraction between the soil particles and the object, and partly to the adhesive action of the water in the soil. The predominance of the latter mechanism has been postulated by Nicholls (1929) and generally accepted ever since. Strong solid/solid attraction is,

however, theoretically possible (De Bruyne and Houwink, 1951), and recent work has shown the existence of many examples of this type of adhesion. There is, for instance, evidence that strong adhesion occurs between two metal surfaces pressed tightly together, but it is not normally detected because as soon as the pressure is removed the joints are broken by the elastic recovery which takes place. If materials are used which do not recover appreciably (e.g. indium), substantial adhesions can be detected (Tabor, 1952). These experiments suggest an analogy with the behaviour of soil which can be very sticky when moist, and consequently easily deformable but quite non-adhesive when dry and elastic. The investigation described here was intended to establish the relative importance of solid/solid attraction and the adhesive action of the soil water.

Hypotheses on the adhesive action of water

For simplicity two distinct types of *water* linkage are postulated, as shown diagrammatically in Figs. 1 and 2.

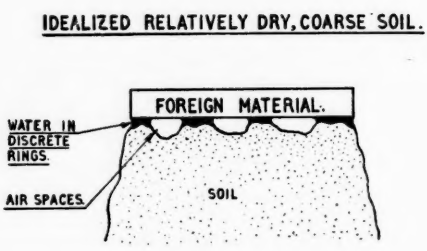

FIG. 1.

The case shown in Fig. 1 might be expected with a relatively dry and coarse soil. The surface of the soil is pictured as a series of little pinnacles —the corners of individual soil particles or aggregates—and these are stuck to the foreign material by discrete rings of water. The adhesions at each individual joint may be evaluated from its cross-sectional area and the curvature of the air/water meniscus (McFarlane and Tabor, 1950). This mechanism is similar to that suggested by Haines (1925) and Fisher (1926) for the cohesion of soil. It would appear from Schofield's work (1938) that ordinary surface-tension laws can still be applied, even if the water films are only a few molecules thick. There is a possibility of water-dipole/cation bridges in the water films, of the type suggested in Russell's theory of soil cohesion (1934), but the existence of these would, presumably, be reflected in the surface tension. The experiments of McFarlane and Tabor on the adhesion of a small glass sphere to a plane surface are in excellent agreement with the surface-tension theory. A sphere was used because it was convenient experimentally, but there seems no reason to doubt that the results could be applied to more irregular shapes, such as pinnacles on a soil surface.

Since the angle of contact of the water on the surface of a foreign material will influence the curvature of the meniscus, the 'wettability' of the material will influence the magnitude of the adhesion where the pinnacle theory holds.

FIG. 2.

The second type of water link (illustrated in Fig. 2) is of greater practical importance since it is likely to occur at moisture contents at which soils are normally said to be sticky. In this case there is a water film between the plate of foreign material and the soil, and this film, though unlikely to be absolutely continuous, is connected with the bulk of the soil water through channels between the surface layer of soil particles. If the system is allowed to come to equilibrium the water will move until it is under the same tension throughout. To achieve this, most of the water/air menisci will move into channels whose dimensions naturally give the same tension, but some of the menisci may have to assume a 'forced' curvature because they are unable to reach channels of the appropriate size. Thus, once equilibrium has been reached, the water link will give an adhesive strength per unit area of water film equal to the moisture tension. In this case the size of the angle of contact between water and the material stuck to the soil will not affect the adhesion, provided it does not exceed 90°. If an attempt is made to measure the adhesion by pulling off the plate of foreign material rapidly, the equilibrium will be disturbed. This may result in the air/water menisci in the immediate vicinity of the plate moving in such a way as to increase the water tension locally and the adhesion will thus be increased. If the load is applied sufficiently slowly, however, water will pass from the bulk of the soil to the water film at the joint and the adhesion will not rise. Eventually a stage will be reached where movement of the plate is not accompanied by a local increase in moisture tension, and then failure will occur.

There is also another reason why speed of loading may influence the value obtained in adhesion tests. For simplicity, consider the water film involved in the adhesion as lying between two parallel plane surfaces, one the soil solid, and the other the foreign material. If a load is applied to the joint, perpendicular to the plane of the surfaces, no appreciable movement will occur until the surface-tension forces have been overcome.

Once movement has started its rate will be limited by the viscosity of the water. Assuming water to be a Newtonian liquid, and both solids to be equally wettable, the time necessary for complete failure to occur will be $3\eta V^2/8\pi FD^2$, according to Healey (1926) and De Bruyne and Houwink (1951), where η = coefficient of viscosity of water,

V = volume of water,

F = load applied,

D = initial distance between plates.

Thus, if a high rate of loading is used in an adhesion test, the load may reach a value far in excess of that required to overcome surface-tension forces before *complete* failure occurs. In MacFarlane and Tabor's experiments with a glass sphere and water, referred to above, the speed of loading was slow enough to avoid anything but a negligible increase in adhesion on the value predicted from surface tension. With other liquids possessing a far higher viscosity/surface tension ratio than water, substantial increases were encountered. It is thought likely that, with the speed of loading used, the viscosity effect would also be negligible in adhesion tests with soil dispersed in water. This is borne out to some extent by experiments described by Fountaine (1953) in which loads were increased at different rates in soil/metal adhesion tests with no significant change in the values obtained.

Experimental

The effect of the nature of the foreign material on adhesive strength

The first experiments carried out were to determine the effect of varying the materials of which the test plate was made. The tests were made with the soil-adhesion meter described by Fountaine (1953). The soil samples were puddled into a ring of diameter 5 cm. and thickness 1 cm. and extruded from this into the apparatus. The test plate was loaded on to the soil either with a known load for a given time or until the soil sample had deformed to a predetermined thickness fixed by a stop on the apparatus. Six different materials, each polished as nearly as possible to the same degree, were used in these experiments and the conditions and results are given in Table 1. The load required to pull the plate off the soil was provided by running water into a vessel, and the rate of flow was such that it took 25 seconds to cause failure in a joint with a strength of 100 g./sq. cm.

These experiments provide some evidence that direct attraction between the soil particles and the material of the test plate contributes little to the adhesive strength. This is deduced from the similarity in the adhesion of soil to such diverse materials as chromium and paraffin wax. The inevitable scatter of the results would, of course, hide any small changes due to varying the material, but the experiments did suggest that water played a major part in adhesion. The soil used for these experiments was in such a state that the wettability of the test plate was

unlikely to affect the magnitude of the adhesion caused by surface-tension effects (i.e. the water film at the soil/metal interface was believed to be in contact with the bulk of the soil water as in Fig. 2). If it is assumed that the rate of loading is sufficiently slow for viscosity effects to be negligible, the contribution of water to the joint strength is presumably that due to the intermolecular forces reflected in surface-tension phenomena.

TABLE 1

Effect of Material on Adhesion

Adhesions (g./sq.cm.)

Plate pressed on with load of 11,590 g. for ½ min.				*Constant deformation (thickness reduced from 1 cm. to 0·85 cm.*			
Clay soil just below sticky point		*Clay loam just below sticky point*		*Loam just below sticky point*			
Chromium	*Paraffin wax*	*Chromium*	*Aluminium*	*Chromium*	*P.V.C.*	*Perspex*	*Polythene*
248	230	186	197	63	68	73	58
265	246	212	215	58	69	69	59
281	257	217	209	66	73	59	71
260	251	220	211	73	66	63	63
263	234	210	213	71	72	67	61
246	263	218	224	67	64	68	68
Mean 260½	247	210½	211½	66	69	66½	63

For the next experiments coarser materials were used which were expected to adhere to the test plate in a manner approximating to the first mechanism suggested above (Fig. 1). The first material used was Leighton Buzzard sand. The values of adhesion were, of course, very much lower than before, and the adhesion meter was too insensitive. The tests were therefore made with a modified laboratory balance, in which one pan was replaced by the test plate. Brass and paraffin-wax plates were used and the results (Table 2) indicate that the wettability of the

TABLE 2

Constant Deformation Tests on Coarse Materials
(Thickness reduced from 10 mm. to 8·5 mm.)

Adhesions (g./sq.cm.)

Builders' sand Moisture content				*Sandy soil Moisture content*					
9%		*18%*		*10½%*		*13½%*		*17%*	
Wax	*Brass*	*Wax*	*Brass*	*Wax*	*Brass*	*Wax*	*Brass*	*Wax*	*Brass*
0·46	1·38	1·74	3·09	1·38	1·71	2·60	3·55	3·42	4·10
0·41	0·72	1·81	2·88	1·02	2·30	1·74	3·77	2·37	4·90
0·18	0·66	1·91	2·80	1·56	2·70	2·55	3·22	2·53	4·33
0·99	1·07	1·74	2·55	1·07	1·84	3·34	4·55	3·73	3·82
0·38	0·61	2·14	2·78	1·02	1·68	2·91	3·19	2·65	3·75
Mean 0·48	0·89	1·87	2·82	1·21	2·05	2·63	3·66	2·94	4·18

plates influenced the adhesion. Unfortunately a large scatter in these experiments appeared inevitable. Further tests were carried out with a coarse sandy soil at low moisture contents and again the paraffin-wax plate gave lower adhesions (Table 2). A clay loam soil, however, even at a moisture content as low as 22 per cent. did not show any difference (Table 3) presumably because the mechanism of adhesion was closer to the second mechanism postulated above (Fig. 2).

TABLE 3

Constant Deformation Tests on Relatively Dry Heavy Soil
(Thickness reduced from 10 mm. to 8·5 mm.)

Adhesions (g./sq.cm.)

Clay loam soil Moisture content 22%	
Wax	*Brass*
9·2	9·4
8·9	8·2
9·4	9·6
9·7	10·1
9·2	9·7
Mean 9·3	9·4

The effect of different dispersion liquids on adhesive strength

The next experiments were intended to show how much of the adhesion could be accounted for by surface-tension effects. Comparison of the adhesions of soil pastes dispersed in a variety of liquids shed little light on the problem, mainly because pastes of comparable composition by volume had quite different rheological properties. They therefore behaved quite differently when the test plate was pressed on to them. The same trouble occurred with various artificial 'soils' such as mixtures of kaolin and sand, but pastes of carborundum powder dispersed in different liquids did possess somewhat similar rheological properties. This was presumably because the carborundum packed in the same way irrespective of the dispersing liquid, and because the liquids chosen all wetted the carborundum to approximately the same degree. Table 4 shows the adhesions of the various pastes to a chromium-plated plate, and it will be seen that the adhesions are roughly proportional to the surface tensions. No extensive work was done with these pastes, however, because they were so far removed from soil, and also under all conditions the failure that occurred in the adhesion meter was rather unsatisfactory in that the test plate was always contaminated with some carborundum. Thus pure adhesion was not being measured.

The next approach was to modify the surface tension of water with a surface-active agent of the alkyl sulphonate type (Teepol). It was found that this agent would halve the surface tension of the water without affecting its viscosity appreciably. Pastes of soil dispersed in water and Teepol solutions of various strengths (up to 2 per cent.) appeared similar

rheologically, but the technique was abandoned because soil was found to have a large capacity for sorption of surface-active materials and the reduction in surface tension did not persist once the solutions were mixed with soil.

TABLE 4

Adhesion of Carborundum Dispersions (*g./sq.cm.*)

(*Constant Load Tests, 11,590 g.*)

Dispersion liquid		
Water	*Nitrobenzene*	*Alcohol*
81	38	21½
80	29½	21
77	32½	23½
92	40	22½
89	32	23½
Mean adhesion 84	34½	22½
Surface tension dynes/cm. 73	44	23

Adhesion tests with controlled moisture tension

Since it was found impossible to vary the surface tension of the dispersion liquid in the soil paste, other methods of varying the moisture tension within the soil were sought. The technique finally used was similar to that normally used in determining the moisture-characteristic curve of soils (Haines, 1930). The soil was packed into a sintered glass Buchner funnel and the water within it could be brought to any desired tension by adjusting the height of a U-tube filled with water which was attached to the funnel. For the adhesion experiments the soil was saturated, and thoroughly puddled, and a plate of the foreign material being studied was pressed on to its surface. The U-tube was set to give the desired moisture tension and time allowed for equilibrium to be reached. This occurs when all the air/water menisci, including those in the vicinity of the test plate, have assumed the appropriate curvature to hold up the column of water in the U-tube. To measure the adhesion between the plate and soil the Buchner funnel was inverted and the apparatus arranged as shown in Fig. 3. The soil was scraped away from the edges of the plate with a small spatula, as shown in the diagram, so that no friction occurred between the soil and the plate, and so that failure could occur more easily at the soil/metal interface than at the soil/glass interface. A 3-cm. Buchner funnel was used, and a brass plate of diameter 2·5 cm. Approximately 3 mm. depth of soil was placed in the funnel.

To determine the time necessary for equilibrium to be reached, the test plate in a number of funnels was replaced by the sintered end of a glass immersion filter connected to a manometer so that the time necessary for the moisture tension to rise to the required value could be measured. The first soil used was a clay loam. Experiments with the

immersion filter showed that this soil took up to 2½ days to come to equilibrium at 20 cm. moisture tension: the maximum it was proposed to use. For the adhesion test the samples were, therefore, allowed at least 4 days to come to equilibrium in case any of them should be somewhat

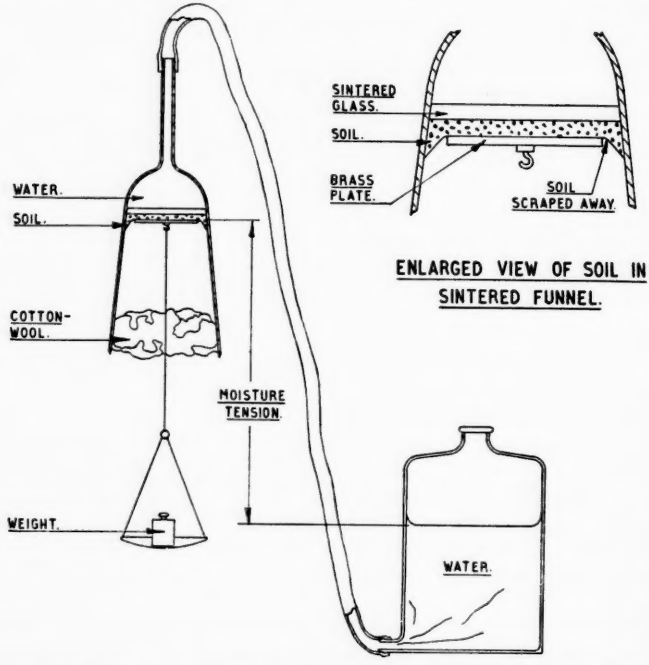

FIG. 3.

less permeable than those used for the trial. So that evaporation did not occur too rapidly for equilibrium to be reached, the Buchner funnels were closed with corks, each perforated by a capillary tube to maintain the air above the soil at atmosphere pressure. To measure the adhesion the corks were removed and the water was run into a vessel attached to the plate from a jet delivering 350 c.c. per minute. The results are shown in Table 5. In this table the actual results are shown alongside the adhesions which would have been measured if the surface of the plate had been entirely covered with water under the requisite tension, and if the adhesion per unit area had been equal to the moisture tension. In fact the adhesions recorded were greater than the theoretical value, but not by a consistent factor. This was ascribed mainly to a local increase in moisture tension in the neighbourhood of the plate when the load was applied. The rate of loading was apparently too great to allow

time for water to percolate through the soil to restore the moisture tension to the value determined by the U-tube. This accounts for the observation that, in roughly half the tests, failure occurred at the sintered glass/soil interface, not at the metal/soil one. Presumably the moisture tension is kept down at the surface of the sintered glass, through which the water can move relatively quickly, and failure takes place here even though some shearing of the soil is also entailed. Further experiments revealed that the adhesions fell off at slower rates of loading, and to obtain the minimum value with this soil the load had to be gradually increased over a period of about 2 days.

TABLE 5

Adhesion of Clay Loam Soil in Preliminary Tests

Moisture tension (cm. of water)	4·2	6·3	8·3	9·7	11·7	13·7	15·7	19·1	21·0	23·0
Adhesion (g./sq.cm.)	59	94	113	115	115	90	87	123	133	142
Theoretical adhesion (g./sq.cm.)	20·7	31·0	40·8	47·7	57·5	67·4	77·3	94·0	103·3	113·2

In the light of these investigations the following experiment was carried out on the adhesion of the clay loam soil. Sixteen soil samples were prepared in Buchner funnels as before and brought to equilibrium at moisture tensions of from 2 to 17 cm. inclusive. To be quite safe, 1 week was allowed for equilibrium to be reached. The plates were then loaded with brass weights representing 75 per cent. of the theoretical adhesion in each case, and left for 2 days. To minimize evaporation cotton-wool was placed loosely inside the Buchner funnels. After 2 days none of the plates had fallen off. Small increments in weight, ranging from 0·2 g. for the 2-cm. moisture tension sample to 2 g. for the 17-cm. sample, were then added every 2 hours or after an overnight interval, until failure occurred. In every case the plate was quite clean after failure. The results of the experiment are shown in Fig. 4, which is a graph of adhesion against moisture tension. The line shown is the theoretical straight line which should be obtained if the adhesion were due entirely to the moisture tension within a perfectly continuous water film. In this experiment in addition to the 2-hour pauses between increments, two overnight intervals were allowed, the last when the loads were about 5 per cent. below the theoretical value. The deviations from the line are nearly all within the limits of experimental error. The moisture tension could only be fixed within 2 mm. of the required values due to imperfections in the sintered glass, difficulty in fixing the sintered surfaces absolutely level, and inaccuracy in judging the exact position of the metal/soil interface. The size of the weight increments could also give rise to about 3 per cent. error.

The experiment was repeated with a sandy loam soil and a sand and the points shown in Figs. 5 and 6 were obtained. The sand gave scattered results below the theoretical line over the whole moisture-tension range, while the sandy loam only diverged seriously from theory at the higher tensions used.

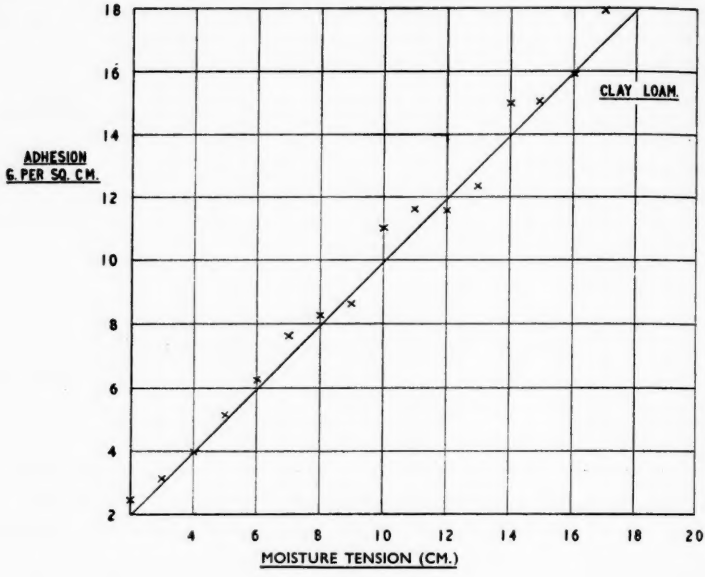
CLAY LOAM.
ADHESION
G. PER SQ. CM.
MOISTURE TENSION (CM.)
2
4
6
8
10
12
14
16
18
20

FIG. 4.

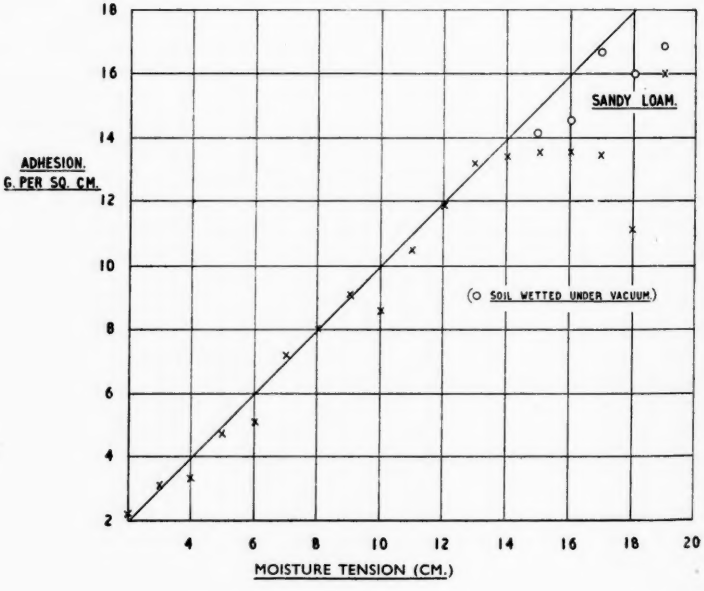
SANDY LOAM.
(o SOIL WETTED UNDER VACUUM)
ADHESION.
G. PER SQ. CM.
MOISTURE TENSION (CM.)
2
4
6
8
10
12
14
16
18
20

FIG. 5.

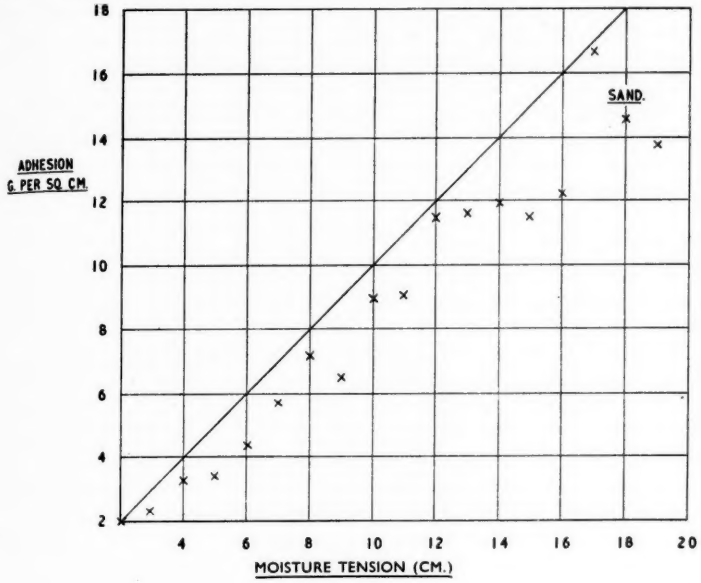

FIG. 6.

The cause of the anomalous values for adhesive strength

To find out how many of the anomalies could be accounted for by discontinuity of the water film, observations were made with a low-powered binocular microscope through a glass plate. For this purpose a layer of about 2 mm. of soil was deposited on the sintered glass end of an immersion filter and the glass plate pressed on to it. With the clay loam soil a virtually continuous water film could be seen, even when the water was under 18-cm. tension. The sandy loam soil also gave a continuous water film when small tensions were applied, but at about 13-cm. tension small bubbles appeared in several places and these enlarged as the tension was increased. This observation agreed remarkably well with the results in Fig. 5 which shows a deviation of the observed from the theoretical adhesion at about 14-cm. tension. It seemed possible that the occurrence of this type of discontinuity might be delayed if as much air as possible were removed from the soil before the experiment by wetting it under vacuum. It had been hoped to give the vacuum treatment with the test plate in position, but this proved impracticable because the upheavals which took place under vacuum invariably disturbed the plate. Five samples of the sandy loam soil were wetted under vacuum and slightly higher adhesions were obtained, as shown in Fig. 5. With the sandy soil a complete moisture film was not observed even at moisture tensions as low as 3 cm. It was very difficult to prepare a really flat surface on this soil and, evidently, sufficiently large cavities

were always left for them to be unable to hold water at even small tensions. The soil itself was found to release little water at tensions of less than 10 cm., but it appeared difficult to place the test plate on to the soil without leaving some cavities bigger than the biggest soil pores. With the sandy soil the periphery of the water film was nearly always irregular and lay some way inside the circle which was being considered theoretically. Wetting this soil under vacuum had no consistent effects on the adhesions obtained.

Rapid loading tests

Other tests were carried out on the same three soils under the same conditions as before except that the load was applied rapidly by running water into a vessel attached to the test plate at the rate of 350 c.c./min. The total weight of the vessel itself and the test plate was 4·9 g. In Table 6 below the results of these tests are given alongside those obtained at the same tensions using the slower loading technique. These results were of little value from the theoretical point of view, since no measurements were made of permeability, or local moisture tension increases, but they are of practical interest since the rate of loading used may be regarded as more realistic than in the previous tests.

TABLE 6

Adhesion in Rapid Loading Tests (g./sq.cm.)

Moisture tension (cm. of water)	*Clay loam*		*Sandy loam*		*Sand*	
	Slow	*Rapid*	*Slow*	*Rapid*	*Slow*	*Rapid*
3	3·1	5·2	3·1	5·7	2·3	5·9
6	6·2	14·2	5·1	9·8	4·4	8·1
9	8·6	20·9	9·1	11·0	6·4	10·2
12	11·6	20·4	11·8	12·4	11·4	12·8
15	15·0	18·3	13·5	15·7	11·9	17·7

Conclusions

1. The adhesion between the soils and foreign materials used in the experiments described can be attributed entirely to the water film between the joined surfaces.

2. Within the 'sticky' range at any rate, the value of the adhesion (within the limits of the experimental error) was found to be equal to the product of the area of the water film joining the two surfaces and the tension within it.

3. Rate of loading appeared to affect the adhesive strength only in so far as it determined the length of time available for water to move into the film at the joint when a local increase in moisture tension occurred.

4. Solid/solid attraction plays an insignificant part in the adhesion. The nature of the foreign material is, therefore, of no consequence unless it is completely non-wetting or the soil exceptionally dry and coarse.

Acknowledgements

The author is most grateful for the help received in this work from Dr. E. W. Russell of Oxford University, Dr. D. Tabor of Cambridge University, and Dr. R. Kenworthy Schofield and his staff at Rothamsted Experimental Station.

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(*Received 30 September 1953*)

FIXED AMMONIA IN TROPICAL SOILS

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I. *Introduction*

In an earlier paper Hardy and Rodrigues (1951) have demonstrated the accumulation of large amounts of ammonia in simple exchangeable form in certain sugar-cane soils of British Guiana. These accumulations were first revealed by the extremely low values obtained for carbon-nitrogen ratio in the lower horizons of certain soil profiles but, even in the topsoil layer (0–6 in.), the equivalent of as much ammonia as that present in a ton of ammonium sulphate per acre was found. Most of the British Guiana soils have been growing sugar-cane for many decades and some have received in the course of time considerable dressings of ammonium sulphate, a portion of which may have been retained in exchangeable form as ammonium-ion. This does not necessarily explain the large amount of exchangeable ammonia found in all cases; some may have been produced by the decay of swamp residues.

The British Guiana sugar-cane soils are not unique in the Caribbean Region in showing abnormally low values for carbon-nitrogen ratio in subsoil layers. The phenomenon is common among the soils of this region, and is not confined to agricultural soils receiving fertilizer treatments, nor is it always simply explained by the accumulation of ammonium-ion in the soil in readily exchangeable form. The investigation to be described is a preliminary attempt to discover the cause of diminishing carbon-nitrogen ratio with depth, and to examine the nature of ammonium-nitrogen absorption.

II. *Carbon and Nitrogen Relationships in Sandy and Clayey Soil Profiles*

In Table 1 are set out typical laboratory data obtained by routine analysis of profile samples representing sandy and clayey soil types occurring in Trinidad. They show the typical diminution with depth of the value for carbon-nitrogen ratio. The data are characteristic of a large number of soil profiles widespread in the British Caribbean Region.

Methods of analysis. (1) Sand was determined by the conventional International sieve-and-beaker method. (2) Reaction was determined by the glass electrode. (3) Carbon was estimated by a wet combustion method (Hardy and Rodrigues, 1949), using a mixture of chromic acid and sulphuric acid at 100° C. and collecting and measuring the gaseous products in a nitrometer over mercury. Nitrogen was determined by the standard Kjeldahl method, using a copper catalyst. The third decimals in the data for carbon are not significant, but are retained for convenience in calculating the C/N ratio.

Discussion of carbon-nitrogen data. Scrutiny of the experimental data set out in Table 1 reveals the following important facts regarding the carbon-nitrogen relationships of the soils examined.

TABLE I

Data for Carbon and Nitrogen Contents of Typical Soil Profiles (Tumpuna Forest Reserve)

Lower depth (in.)	Sandy soil							Clayey soil						
	Arena sand							Ecclesville clay						
	Soil No.	Sand (2·0 0·2) (%)	Silt + clay (%)	Reaction (pH)	Total C (%)	Total N (%)	C/N ratio	Soil No.	Sand (2·0 0·2) (%)	Silt + clay (%)	Reaction (pH)	Total C (%)	Total N (%)	C/N ratio
	TUM							TUM						
6	59	93	7	4·2	0·648	0·046	14	112	34	66	4·6	1·192	0·165	7
12	60	92	8	4·2	..	..	..	113	..	..	4·6	..	..	..
18	61	92	8	4·1	0·320	0·023	14	114	46	54	4·8	0·275	0·082	3
24	62	90	10	4·3	..	..	..	115	..	..	4·7	..	..	..
36	63	90	10	4·1	0·203	0·019	11	116	39	61	4·6	0·162	0·071	2
48	64	87	13	4·4	..	..	..	117	..	..	5·1	..	..	..
60	65	88	12	4·9	0·216	0·018	12	118	41	59	7·1	0·084	0·063	1
72	66	90	10	5·0	..	..	..	119	..	..	7·4	..	..	..

1. The total carbon and the total nitrogen contents of corresponding layers show a more uniform distribution of organic matter down the profile of the sandy soil as compared with the clayey soil.
2. The diminution of the carbon-nitrogen ratio with depth is much more marked in the clayey soil profile than in the sandy soil profile, reaching extremely low values at depths below 12 in.
3. The magnitude of the carbon-nitrogen ratio is much higher in the several layers of the sandy soil profile as compared with those for corresponding layers of the clayey soil profile.
4. The fact that the ratio values, calculated from carbon and nitrogen contents determined by conventional methods of soil analysis, are much lower in the clayey soil suggests that a considerable proportion of the actual nitrogen, possibly as ammonium-ion, occurs in a highly stable and firm combination with the clay mineral component.

III. *The So-called 'Fixation' of Ammonium-ion by Soils: Review of Recent Literature*

The fact that nitrogen in the form of ammonium-ion may be absorbed by soils and 'fixed' much more firmly than by the simple base-exchange process has been repeatedly demonstrated by various soil chemists in recent years. Thus McBeth (1917) has reported the absorption from added ammonium salts of large amounts of ammonium-ion which resists extraction by 10 per cent. hydrochloric acid. Chaminade (1940) found that such absorbed ammonium-ion, though not replaceable by potassium-ion in neutral potassium chloride solution, was rendered replaceable after prolonged grinding, and was directly extractable by treatment with hydrofluoric acid. More recently Stanford and Pierre (1946), Bower (1950*a*), Barshad (1951), and Allison, Doetsch, and Roller (1951) have established what has therefore been termed the 'fixation' of ammonium-ion in difficultly-exchangeable form by certain clay minerals, chiefly belonging to the illite, vermiculite, and montmorillonite types, and its essential similarity to the well-known fixation of potassium-ion by clays. Bower (1950 *b*) found that sodium-ion under certain circumstances is

somewhat more effective than potassium-ion in displacing fixed ammonium-ion in clay soils, and Barshad (1951) has suggested that the difference between the quantitative values for ammonia released by distillation of the soil with sodium hydroxide and that released by potassium hydroxide might furnish a measure of the capacity of the soil for fixing ammonium-ion. Bower (1950 *b*) found also that, whereas most of the ammonium-ion absorbed by soils in the readily-exchangeable form is nitrifiable, fixed ammonium-ion is nitrified only to the extent of 13 to 28 per cent. Allison *et al.* (1951), however, obtained a lower value for the nitrification of fixed ammonium-ion, namely, less than 10 per cent.

Concerning the different kinds of nitrogenous compounds that occur in soils, Mattson and Koutler-Andersson (1943) have suggested that that part of the organic nitrogen present in soil which is stable to hydrolysis by strong acids and alkalis, may occur as nitrogenous complexes formed by interaction between oxidized lignins and ammonia. They demonstrated that lignin was able to fix ammonium-nitrogen in non-exchangeable form under conditions obtaining in the soil.

IV. *Experimental Work*

Materials

Soil samples taken from four soil profiles that show the characteristic fall in carbon-nitrogen ratio with depth were examined in detail in this investigation. The first two soils (Nos. I and II) have developed over river alluvium in Stann Creek Valley, British Honduras. The parent rock is muscovite granite. The alluvium comprises fine sand and silt made up mainly of quartz and mica (possibly hydrous) with much kaolinite. These soils may be classed as Yellow Podzolic, though they occasionally receive surface additions of fresh alluvium during floods.

The third soil (No. III) occurs on a valley slope near Toco in the Northern Range of Trinidad. It is developed over colluvium derived from calcareous schist. It consists mostly of fine quartz with some finely divided sericitic mica and kaolin, highly saturated by exchangeable calcium. It resembles Rendzina in that the topsoil is black and highly humic with over 3 per cent. organic matter in the top 15-in. layer.

The fourth soil (No. IV) occurs on the east bank of the Demerara River at Providence Sugar Estate, British Guiana. It is developed over river levée alluvium (Riverside Silt) comprising quartz, kaolin, and possibly finely divided mica, derived from basement metamorphic and igneous rocks. It might be classed as Yellow Podzolic, though the presence of a gley layer below 24 in. suggests that it might better be described as Low Humic Gley.

Fractionation of the nitrogenous component

Total carbon and total nitrogen were determined on all the soil samples by methods described in a previous section. In addition the following procedures were used in an attempt to fractionate the combined nitrogen, assuming it to be ammonium. Before analysis the soil

samples were ground in a mill so that at least 80 per cent. passed a 100-mesh sieve.

i. *Exchangeable ammonium.* This was determined by repeatedly washing 1 g. soil with normal potassium-chloride solution, acidified to pH 1·0 with hydrochloric acid.

ii. *Ammonium extractable by hydrofluoric acid.* This was determined by mixing 1 g. soil with 1 ml. of 50 per cent. sulphuric acid and 4 ml. of hydrofluoric acid in a platinum dish. After standing 1 hour the supernatant liquid was decanted and the residue washed with water in a centrifuge. Ammonia was then distilled off from an aliquot of the extract by the Markham micro-distillation method after driving off the hydrofluoric acid in the presence of sulphuric acid.

Results

The experimental results obtained by the application of the methods of nitrogen fractionation described above are presented in Table 2.

TABLE 2

Data for Nitrogen Fractionation of Selected Soils

		1	*2*	*3*	*4*	*5*	*6*
Soil No.	*Depth (in.)*	*Total* N (%)	C/N *ratio*	*Exch.* NH_4–N (%)	HF–*extr.* N (%)	C/N *ratio (corrected)*	HF–N (% *total* N)
				I. *British Honduras Soil (A)*			
BHA							
383	4–10	0·199	9	0·006	0·053	12	26·5
384/5	26–42	0·079	3	0·001	0·048	7	60·8
386	54–60	0·088	1	0·002	0·069	7	78·4
				II. *British Honduras Soil (B)*			
BHA							
338	0–6	0·238	9	0·004	0·034	10	14·3
339	24–30	0·055	8	0·0025	0·016	12	29·1
340	54–60	0·033	8	0·001	0·015	16	45·5
				III. *Trinidad Soil*			
CB							
137	0–6	0·308	9	0·001	0·113	14	36·7
138	6–15	0·213	9	0·005	0·099	16	46·5
139	15–21	0·204	3	0·004	0·150	10	73·5
				IV. *British Guiana Soil*			
BG							
228	0–18	0·128	10	0·0015	0·0415	15	32·4
230	23–28	0·058	4	0·008	0·0335	14	57·8
232	40–50	0·054	3	0·005	0·034	9	63·0
234	53–66	0·154	2	0·084	0·022	5	14·3

Discussion. Comparison of the data for exchangeable ammonium-ion (column 3) with those for total nitrogen (column 1) indicates that (except for the British Guiana soil (No. IV) which may have received heavy dressings of ammonium sulphate fertilizer) only a small proportion of the

total nitrogen present is easily exchangeable. On the other hand, the amount of ammonium-nitrogen released by hydrofluoric acid treatment (column 4) is relatively high, in some cases as high as 75 per cent. of the total nitrogen (column 6). In each set of profile samples the absolute value of the hydrofluoric acid-extractable nitrogen (column 4) remains fairly constant throughout the profile, but its relative amount, expressed as a percentage of the total nitrogen, increases greatly with depth, presumably because, in the upper layers, much of the nitrogen is not combined or fixed by clay minerals. When allowance is made for this fraction, the numerical values for carbon-nitrogen ratio are raised appreciably (column 5; compare column 2). The 'corrected' values now show the same order of magnitude as those of a sandy soil.

In order to learn more about the nature of the hydrofluoric acid-extractable nitrogen fraction, further determinations were made, as follows.

iii. 'Fixed' ammonium was next measured in some of the samples by displacement of ammonium-ion by sodium-ion and by potassium-ion, employing acidified (pH 1·0) normal solutions of sodium chloride and potassium chloride respectively, at room temperature. The results obtained are given in Table 3.

TABLE 3

Data for Exchangeable Ammonium

Soil No.	NaCl-*extracted* % N	KCl-*extracted* % N
I. *British Honduras Soil (A)*		
BH 383	0·0060	0·0055
384/5	0·0010	0·0010
386	0·0020	0·0025
II. *Trinidad Soil*		
CB 138	0·0065	0·0055

Discussion. The data for ammonium-ion replaceable by sodium and by potassium do not show much difference in the reactivity of those two ions for replacing ammonium-ion under the conditions of the experiment. In either case, the amount of displaced ammonium is small.

iv. 'Fixed' ammonium-nitrogen, released by hydrofluoric acid treatment, was next determined on some samples that had previously been oxidized with hydrogen peroxide (20 vol.) followed in two cases by treatment with chromic acid-sulphuric acid mixture at 100° C. (as used in the wet combustion method for estimating total carbon), in order to ascertain whether the organic component of the soil might be the source of this 'fixed' nitrogen. It is possible, should this actually be the case, that the treatment of a soil with hydrofluoric acid in the presence of sulphuric acid might bring about, at the high temperatures developed, appreciable hydrolysis of the organic component so as to liberate ammonia gas. The results are given in Table 4.

TABLE 4

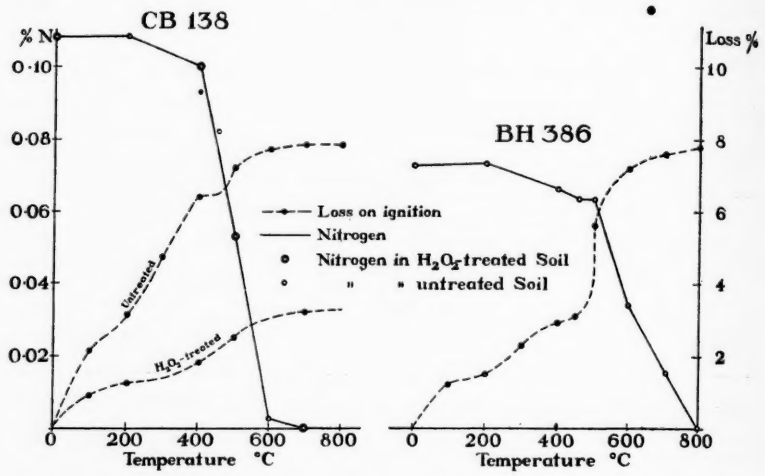
Data for 'Fixed' Nitrogen after Oxidation

Depth (in.)	*Soil No.*	*Original soil*			H_2O_2-*oxidized*			CrO_3 *oxidized*
		Total C	*Total* N	HF-N	*Total* C	*Total* N	HF-N	HF-N
				III. *Trinidad Soil*				
0–6	CB 137	2·62	0·308	0·113	n.d.	0·104	0·098	n.d.
6–15	138	1·80	0·213	0·099	0·04	0·109	0·097	0·100
				I. *British Honduras Soil (A)*				
4–10	BH 383	1·74	0·199	0·053	n.d.	0·062	0·053	n.d.
54–60	386	0·11	0·088	0·069	0·03	0·084	0·064	0·064

Discussion. The data in Table 4 show that oxidation with hydrogen peroxide removed 98 per cent. of the total carbon in one case and 73 per cent. in the other (a deep subsoil containing only a small amount of organic matter). It also removed about 60 per cent. of the total nitrogen in three cases (but only 5 per cent. in the deep sample). In spite of the great loss of nitrogenous organic matter through oxidation, the amount of nitrogen extractable by hydrofluoric acid still remained practically unchanged, which implies that this fraction is firmly fixed in the non-carbonaceous mineral component of the soil, and that it is apparently not affected by drastic oxidation with chromic-sulphuric acid mixture at 100° C.

v. 'Fixed' ammonium-nitrogen, released by hydrofluoric acid treatment, was determined on two soil samples, one (CB 138) containing a fairly large amount of organic matter and the other (BH 386) containing only a small amount, that had previously been heated to different temperatures. In the case of the first sample, the experiment was repeated after organic matter had previously been mostly removed by oxidation with hydrogen peroxide. The results obtained are shown in the accompanying graph. They indicate that heating to 450° to 500° C. may be carried out without causing any appreciable reduction in the amount of nitrogen released by subsequent treatment of the residue with hydrofluoric acid. The curve in the graph showing the fall in nitrogen content lags slightly behind that for loss on heating. In the case of sample BH 386, having low initial organic matter content (0·2 per cent.), the loss-on-heating curve shows a pronounced inflexion between 450° and 500° C., but the main loss of nitrogen took place only above 500° C. In the case of sample CB 138, which contained about 4 per cent. of organic matter, the amount of ammonium-nitrogen extractable by hydrofluoric acid after heating followed a similar curve, no matter whether or not the soil had previously been oxidized by hydrogen peroxide.

Discussion. It is evident from these results that fixed ammonium extractable by hydrofluoric acid is definitely not part of the ordinary organic matter component of the soil but is more likely to be firmly fixed by the mineral component.



vi. Ammonia was determined in the hydrolysed extracts of the same two soils as were used in the last experiment resulting from their treatment with boiling 10 per cent. sulphuric acid under a reflux condenser. Both soils had previously been oxidized with hydrogen peroxide.

The first soil (CB 138, originally rich in organic matter) gave only 0·001 per cent. of ammonia, expressed as nitrogen on the basis of the weight of the original air-dry soil, whilst the second (BH 386) gave only the merest trace of ammonia. Subsequent distillation of the residues with normal sodium hydroxide solution yielded in each case only slightly more ammonia.

Direct prolonged distillation of the two original *untreated* soils with normal sodium hydroxide solution gave 18 per cent. of the total nitrogen content as ammonia in the case of the first soil (CB 138), and 10 per cent. in the second case (BH 386).

Discussion. Evidently simple acid hydrolysis fails to detach an appreciable amount of fixed nitrogen, and more drastic alkaline hydrolysis only detaches ammonia slowly.

V. *Differences between Sandy and Clayey Soils in regard to Capacity for 'Fixing' Nitrogen*

In order to ascertain whether any portion of the nitrogenous component of a *sandy* soil (which presumably does not contain clay minerals) is 'fixed' as a mineral complex released by treatment with hydrofluoric acid, four of the sandy profile soil samples figuring in Table 1, and four of the corresponding clayey soil samples, were examined by this procedure. In the case of the sandy soils it was found that the treatment did not extract any appreciable amount of ammonium-nitrogen. On the other hand, the hydrofluoric acid treatment extracted from each of the four clayey soil samples almost identical amounts of ammonium-nitrogen, namely,

0·045, 0·042, 0·045, and 0·044 per cent.; mean, 0·044 per cent. If these amounts be subtracted from the total nitrogen contents as determined by the Kjeldahl process (Table 1), the numerical values for the carbon-nitrogen ratios down the profile by calculation now become 10, 7, 6, and 4, which are in marked contrast to the original values of 7, 3, 2, and 1. The absence of clay minerals from the sandy soil precludes the possibility of any fraction of the total nitrogen of the sandy soil occurring in a special form of combination with mineral matter.

A further attempt was made to fractionate the total nitrogen present in some of the samples, including a sandy soil, by means of the hydrofluoric acid treatment only, as follows.

The ammonium-nitrogen in the hydrofluoric acid extract was directly determined by distilling with alkali. The remaining nitrogen in the extract was determined by the Kjeldahl method. Also, the nitrogen present in the residue from the hydrofluoric acid treatment was determined by the Kjeldahl method. Knowing the total nitrogen content (Kjeldahl) of the original soil, it is possible thus to construct a 'balance-sheet'. The results are given in Table 5.

TABLE 5

Fractionation of Nitrogenous Components by Hydrofluoric Acid Treatment

		1	2	3	4	5	6	7
			HF-*extract*					
Soil No.	*Soil layer (in.)*	*Total* N (%)	NH_4-N (%)	*Other* N (%)	*Residue*-N (%)	*Residue*-N % *Total*-N	*Sum* (%)	*Recovery* (%)
				Sandy Soil				
TUM 59*	0–6	0·046	0·000	0·028	0·016	35	0·044	95·7
				Clayey Soils				
TUM 112*	0–6	0·165	0·045	0·083	0·036	22	0·164	99·4
118*	48–60	0·063	0·044	0·005	0·022	35	0·071	(112·7)
CB 137†	0–6	0·308	0·124		0·168	55	0·292	94·9
138†	6–15	0·213	0·104		0·107	50	0·211	99·2

* See Table 1. † See Tables 2–4.

Discussion. The data in Table 5 reveal the following facts, certain of which corroborate previous observations.

1. There is no fixed ammonium-nitrogen in the *sandy* soil (column 2), whereas in two of the clayey soils its amount is 27 per cent. and 70 per cent. respectively, of the total nitrogen present. The greater proportionate amount of fixed ammonium-nitrogen occurs in the deep subsoil sample which contains the lesser amount of organic matter.

2. The hydrofluoric-acid extracting agent also removes a considerable amount of nitrogen which is evidently not in the form of ammonium-nitrogen (column 3), amounting to 61 per cent., 50 per cent., and 8 per cent. respectively, of the total nitrogen in the cases of the first three samples. This possibly implies that the hydrofluoric-acid reagent hydrolyses certain relatively unstable nitrogenous compounds (probably amino-acid types) occurring in the soil.
3. The 'residue' nitrogen (column 4), namely that fraction which is *not* affected by the hydrofluoric treatment, presumably being much more resistant, ranges in amount from 22 to 55 per cent. of the total nitrogen (column 5), being highest in the sample having the highest initial total nitrogen content, that is, most organic matter.

General Conclusions

In many tropical soils there appears to occur a large amount of nitrogen which is resistant to ordinary base-exchange methods of extraction, hydrogen peroxide oxidation, chromic-sulphuric acid oxidation at 100° C., and boiling 10 per cent. sulphuric acid, and only comes out slowly with boiling normal caustic alkali. This nitrogen is immediately released in the form of ammonia, however, on decomposition of the soil with hydrofluoric acid, even in dilute solution, when temperatures do not rise too high. The phenomenon is shown, not only by agricultural soils which may have received considerable dressings of ammonium fertilizer, but also by forest soils which presumably have never received such additions.

Where only total nitrogen has been determined in the past, the carbon-nitrogen ratios of certain soils have been found to be abnormally low, but (as results in Table 2 show) when allowance is made for 'fixed' ammonia released by hydrofluoric acid, these ratios attain much higher and more reasonable values. This fixed ammonia is retained by the soil even after the greater amount of the organic matter has been removed by hydrogen-peroxide treatment or by chromic acid oxidation (Table 4).

Mattson and Koutler-Andersson (1943) describe the possible occurrence in soils of certain oxidized lignin compounds capable of fixing large amounts of ammonia but resistant to hydrolysis by strong acids. It is possible that these substances may also be resistant to oxidation with hydrogen peroxide or chromic-sulphuric acid mixture at 100° C., especially if they are firmly attached to the clay mineral structure. If such is the case, hydrofluoric acid treatment may render them more vulnerable to attack by chemical agents. On the evidence so far adduced, however, it is thought that a resistant organic compound of this sort is *not* involved in the fixation of ammonia, as described in the last section, in the case of the Caribbean soils so far examined.

Fixation of ammonium-nitrogen of the kind here considered is usually explained by the penetration of ammonium-ions into the interior of the lattice structure of clay minerals that have the appropriate space dimensions, notably those of the mica type.

The nature of the particular clay mineral which may be responsible for ammonium-nitrogen fixation in the soils examined has not yet been

ascertained, although it may be significant that each has developed from alluvium containing micaceous residues.

An example of a Trinidad Miocene clay soil, known definitely to contain illite and kaolinite in about equal proportions, has been found to contain a relatively large amount of fixed ammonium-nitrogen, actually 76 per cent. of the total nitrogen present. On the other hand, another sample, a Grenada Red Earth soil derived from andesite, in which the clay mineral component is known to comprise solely kaolinite and halloysite, has been found to contain only 8 per cent. of its total nitrogen content in the form of fixed ammonium.

The fraction of total nitrogen here described as 'fixed' occurs in soils under forest where there has been no contamination with ammonium fertilizers. Its magnitude varies from soil to soil but seems to remain appreciably constant within any given profile, thus affecting the carbon-nitrogen ratio considerably more in the lower horizons than in the upper. This, to a large extent, might account for the sudden fall in carbon-nitrogen ratio down the profile so often encountered in tropical soils, notably the more clayey types. In sandy soils the fall is usually much less appreciable throughout. Again, in the fractionation of soil organic matter, a great deal of the reported 'resistant protein' nitrogen fraction should also perhaps be regarded as 'fixed ammonium' nitrogen.

Summary

1. This article describes an investigation into the carbon-nitrogen relationships of certain British Caribbean soils studied in profile.

2. The primary objects were to explain (*a*) why the magnitude of the carbon-nitrogen ratio diminishes rapidly with depth down the profile, (*b*) why the ratio-values are higher in corresponding profile layers for sandy as compared with clayey soils, and (*c*) why the rate of diminution in ratio-value down the profile is greater for clayey than for sandy soils.

3. The procedure followed was to attempt to fractionate the nitrogenous components of certain selected samples that clearly show these relationships by carrying out the following determinations: (i) readily-exchangeable ammonium; (ii) 'fixed' ammonium extractable by hydrofluoric acid; (iii) ammonia differentially liberated by exchange interaction with sodium and potassium hydroxide solutions; (iv) 'fixed' (HF-extractable) ammonium present after oxidation of the soil with hydrogen peroxide and with chromic acid; (v) 'fixed' (HF-extractable) ammonium in unoxidized and oxidized soils heated to 500° C.; (vi) ammonia liberated from oxidized soils by hydrolysis with dilute sulphuric acid at 100° C., and by hydrolysis of untreated soils with normal caustic soda solution at 100° C.

4. The conclusion is drawn from the data obtained that the soils examined contain an appreciable amount of fixed ammonium-nitrogen (ranging from 14 to 78 per cent. of the total nitrogen content) extractable by hydrofluoric acid, presumably present in association with certain clay minerals.

5. The proportionate amount of fixed nitrogen increases progressively with depth down the profile.

6. When the carbon-nitrogen ratio value from the different layers of the profile are 'corrected' by subtracting from the total nitrogen contents the amounts of fixed clay-mineral nitrogen, then (*a*) the corrected carbon-nitrogen ratio values do not diminish as rapidly as before with depth down the profile, (*b*) the corrected values for clayey soils conform more closely with those for sandy soils, and (*c*) the rate of diminution in corrected ratio-values with depth is scarcely greater for clayey than for sandy soils.

7. It is nevertheless possible that the soils may contain small amounts of highly-stable, ammonium-fixing, oxidized-lignin complexes.

8. The identity of the ammonium-fixing clay minerals present in the soils examined was not determined, but the origin and genesis of the soils suggests that it is hydrous mica.

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(*Received 20 June 1953*)

MORPHOLOGY AND CLASSIFICATION OF THE REGUR SOILS OF INDIA

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THE striking features and great extent of the Regur or Black Cotton soils of India have made them of special interest to soil scientists. The soils have therefore been studied extensively, and much thought has been given to their place among the great soil groups of the world. In most studies it has been suggested that the regur is a variety of tropical chernozem (Tamhane, 1950; Desai, 1942; Basu and Sirur, 1938). It has also been suggested that they are like dark clay soils in South Africa (van der Merwe, 1940) and in Australia (Hosking, 1935). Recently Oakes and Thorp (1950) proposed that dark clays of warm regions, including the regur soils, be combined into a single great soil group set apart from those already recognized. That regur is a natural group differing from chernozem is evidently the view of Shokalskaya (1932).

Opportunities for the field study of the regurs of India and of similar soils on other continents by the same scientists have been limited. Comparisons of the regur soils, largely on the basis of laboratory data, have been made by van der Merwe (1940) with soils in South Africa and by Hosking (1935) with soils in Australia. Wadia (1945) cites comparisons of the regur soils with the adobe clays of California, apparently based on laboratory studies. The author examined a number of regur soils in the states of Madhya Pradesh (formerly the Central Provinces and Berar), Bombay, and Hyderabad[1] in October 1951. Interpretations of these field observations and of certain laboratory data are presented in this paper as a basis for further comparison of the regurs with related soils in other parts of the world. A special effort is made to indicate relationships of the regur soils to certain great soil groups in the United States, all of which the author has also studied in the field.

Distribution, Climate, and Topography

The dark-coloured, fine-textured soils included in the regur group are dominant elements of the soil pattern in an area of approximately 200,000 square miles in India (Tamhane, 1950; Wadia, 1945). The region of their principal occurrence is the Deccan plateau between 15° and 25° north latitude and 73° and 80° east longitude. They also occur as less important parts of the soil pattern down to the south tip of India, which lies 8° north of the Equator. The area in which regur soils are important but not dominant elements of the soil pattern comprises

[1] Grateful acknowledgement is extended to Indian soil scientists and others who made arrangements for travel by the author in India. Special thanks are due to Drs. S. P. Raychaudhuri, R. J. Kalamkar, J. K. Basu, and A. D. Desai for their help, both in travel arrangements and in discussions. The views expressed in this paper, however, are the responsibility of the author.

approximately 100,000 square miles, half as large as that in which they are dominant. Taken together, the two regions are slightly larger than Texas.

The climate of the regur region ranges from hot and semi-arid in the margins of the Rajasthan Desert (north of the state of Bombay) to hot and humid in the southern tip of India (Kendrew, 1937). Average annual rainfall ranges from 17 to 55 in., with most of the region having 20 to 40 in. Rainfall distribution is markedly seasonal, 60 per cent. or more of the total falling during the four months June–September. The average annual temperatures are near 75° F., and there is some seasonal variation. On the whole, the region is hot and dry in the early summer. The moderate rainfall and relatively high temperatures are reflected in the native vegetation, thought to have originally been an open 'dry deciduous' or tropical thorn forest with much interspersed grass (Champion, 1936), probably akin to the thornbush savannah in Africa.

The Deccan plateau, which includes the major areas of regur soils, lies mainly at altitudes between 1,000 and 2,000 ft. above sea-level, more of the plateau being near the lower than the upper limit. The plateau is a broad plain with low relief, local differences in elevation (as, for example, those within a square mile) being measurable generally in feet rather than in tens of feet. The gently undulating land surface consists of a succession of low ridges with broad crests that are separated by shallow valleys, often fairly wide. Long gentle slopes lead down from the ridge crests to the valleys, and the land surface seems to run in subdued waves. Large areas in the states of Bombay, Madhya Pradesh, and Hyderabad are essentially free of slopes with gradients steeper than 8 per cent. The extensive smooth plain is broken in places by belts of hills that rise tens of feet above the general level. This is more common near the margins of the Western Ghats (mountains along the west coast) and along the Aravalli Range, but belts of low hills occur out in the broad plain as well. In places the plain is broken by steep slopes leading down into the valleys of major streams cut below the general level. For the most part, regur soils occur in landscapes with long slopes falling between 1 and 8 per cent. in gradient. Where topography is rolling to hilly, the regurs seem to be far less important parts of the soil pattern. Field observations made by the author also suggest that regur soils are unimportant in strongly rolling landscapes and largely absent from hilly ones.

Soil Parent Materials

The regurs have been formed mainly from the Deccan trap (Tamhane, 1950; Wadia, 1945; Bal, 1935; Basu and Sirur, 1938) which, according to Wadia (1939), is chiefly augite-basalt. The Deccan trap seems comparable in many ways to the extensive basalt formations of the Columbia plateau in Washington, Oregon, and Idaho. It ranges in texture from a vitreous basalt at one extreme to a coarse-grained dolerite at the other (Wadia, 1939). The Deccan trap formation includes some acid rocks such as rhyolites and trachytes, but regurs do not seem to have been derived from them. Although the regur soils over great areas seem to have been formed from either the Deccan trap itself or alluvium derived from the trap, some have also been formed from other kinds of rocks.

The author saw regur soils formed from limestone, some of which may have been argillaceous, and others apparently formed from syenite, whereas Hosking (1935) reports that they are formed from shales and calcareous clays. Bal (1935) states that regur soils are formed from gneissic rocks, whereas Wadia (1945) also mentions slates and sandstones. The alluvial sediments giving rise to regur soils seem to have been derived largely from weathered basalt or traprock. In some places, however, more than one source of sediment was indicated by the variety of rock species present as pebbles in the alluvium. As a general rule, it appeared that the regur soils had been formed from rocks or unconsolidated sediments that were dominantly basic in character, low in quartz, and slowly permeable upon weathering.

Morphology of Regur Soils

Typical Regur or Black Cotton soils in India are usually dark in colour, low in organic matter, low in chroma, calcareous, mildly alkaline, high in clay, high in cation exchange capacity, decidedly plastic and sticky, and high in capacity to shrink and swell (Tamhane, 1950). The ranges in contents of organic matter, in colour, and in consistence are small, whereas those in clay contents, exchange capacity, and reaction are wider. The extent of cracking as the soil dries, the content of carbonates, and the thickness of solum vary appreciably among soils included in the group.

Description of six profiles are included in this section of the paper to illustrate the ranges in morphological features of the regur soils. These descriptions illustrate the distinctions among the soils as well as similarities in profiles derived from different parent rocks. In the group of six profiles, the first three are derived from traprock (basalt), the fourth is from limestone, the fifth is from alluvium, and the sixth is from colluvium or alluvium. Numbers have been assigned to the profiles for convenience in subsequent discussions.

Each profile description is preceded by a brief statement on the geographic setting, and is followed by a few additional notes. All profile descriptions use the terminology for colour, texture, structure, and consistence outlined in the Soil Survey Manual (U.S.D.A., 1951). Colour of moist soil is given unless otherwise indicated. Consistence terms used without definitions of moisture contents are in accord with conventions in the Soil Survey Manual. Thus, the terms 'soft' and 'hard' refer to dry soil, the terms 'friable' and 'firm' refer to moist soil, and the terms 'plastic', and 'sticky' refer to wet soil. The approximate mean diameters of roughly spherical concretions are indicated by classes corresponding to those for granular peds. Size limits for these classes are: very fine <1 mm., fine 1–2 mm., medium 2–5 mm., coarse 5–10 mm., and very coarse >10 mm.

1. Typical Regur soil from traprock—near buildings on the State Experimental Farm at Achalpur, Madhya Pradesh.

a. Setting. The farm lies near the edge of the very gently undulating plain that comprises the extensive cotton-growing section of western Madhya Pradesh. Hills rising a few hundreds of feet above the level of the plain are within sight to the north

and north-east. Occasional belts or groups of lower hills, usually tens of feet above the general level, occur locally in the plain itself between Achalpur and Amraoti. For the most part, however, local relief is measurable in feet and the slopes are long and gentle. The profile pit was on a very gentle slope with a gradient of about 2 per cent. By far the greatest part of the land is in cultivation.

b. Profile description:

A_{1p} 0–8 in. Very dark greyish-brown (10 YR 3/2) clay; slightly hard, friable, plastic, sticky; moderate medium granular structure; few fine roots; medium and coarse lime concretions common to few; few fine traprock pebbles.

A_{12} 8–30 in. Very dark greyish-brown (10 YR 3/2 to 3/4) clay; hard, friable, plastic, sticky; compound structure of moderate fine blocky peds crushing under some pressure to moderate medium granular peds; few fine roots; few medium lime concretions and fine traprock pebbles.

A_3 30–38 in. Dark greyish-brown (10 YR 4/2) to brown (10 YR 4/3) clay; slightly hard, friable, plastic, sticky; weak fine to medium blocky structure; few fine roots, few medium lime concretions and fine traprock pebbles; this is a gradational horizon from the solum to the weathered rock.

C_{ca} 38–52 in. Mottled light yellowish-brown (10 YR 6/4), light brownish-grey (10 YR 6/2), and pale brown (10 YR 7/2) loam; mottles are fine to medium, distinct, and numerous; soft, friable, slightly plastic; the light-coloured patches seem to be mainly lime accretions; a few roots and a few traprock pebbles. This layer appears to be well-weathered rock with a lime accumulation.

C 52–80 in. Dark yellowish-brown (10 YR 4/4) loam flecked and mottled with light brownish-grey (10 YR 6/2); mottles are distinct, fine to medium, and common; soft, friable, slightly plastic; essentially structureless in place but with weak fine granular peds when removed; few traprock pebbles. This seems to be well-weathered rock.

c. Additional notes. The C_{ca} horizon (upper part of the saprolite or murram[1]) is prominent on two sides of the pit but not on the other two. It is faint or barely evident at the bottom of the solum in a nearby pit in the same soil type. Checking or cracking marks the solum on all sides of this day-old pit. The cracks are 20 to 40 mm. apart and tend to form squares, which suggests that checking operates in the formation of blocky structure in this soil. In the classification used in tax assessment for rural lands, this soil has the local name of Morand I.

2. Regur soil of medium depth from traprock—east and slightly north of buildings on the State Experimental Farm 5 miles east of Betul, Madhya Pradesh.

a. Setting. The farm lies on an extensive plateau in the northern part of the state which is tens to hundreds of feet above the level of the general plain in western and central Pradesh. The surface of the plateau consists of low broad ridges separated by shallow valleys. Slopes are long and gentle, and local relief is measurable in feet. The profile pit was on the upper part of a slope facing to the south-east with a gradient of about 3 per cent. Over much of the plateau, the Regur soils seems to be restricted to lower slopes and concave surfaces. Most of the land is in cultivation.

b. Profile description:

A_1 0–10 in. Very dark greyish-brown (10 YR 3/2) clay; slightly hard, friable, plastic, sticky; mixed moderate medium granular and very fine blocky peds; few medium and coarse lime concretions and few medium black concretions.

[1] The term 'murram', also spelled 'murrum' and 'mooram', is applied by a number of soil scientists in India to weathered and greatly altered country rock (saprolite) beneath the solum. It is used widely for decomposed and partly disintegrated basalt which can usually be crushed with the fingers although the original rock structure is observable in places.

A_3 10–26 in. Dark greyish-brown (2·5 Y 4/2) clay; slightly hard, friable, plastic, sticky; compound structure of strong fine blocky peds that crush readily to moderate medium granular peds; few blocky peds have slick faces; few very fine lime concretions and few medium black concretions.

C_1 26–44 in. Olive-grey (5 Y 4/2) clay; hard, firm, very plastic, very sticky; strong fine to medium blocky peds crushing with difficulty to moderate medium granular peds; slick faces are common on the blocky peds; thickness of horizon varies from approximately 13 to 23 in.

C_2 44–72 in. Variegated light olive-brown (2·5 Y 5/4) and olive-grey (5 Y 4/2) clay which becomes more uniformly light olive-brown in colour with increasing depth; hard, firm to friable, plastic, sticky; weak fine blocky peds that crush under moderate pressure to a mixture of weak very fine blocky and moderate medium granular peds; few very coarse lime concretions of irregular form.

c. Additional notes. A few traprock pebbles are present in all horizons, and they have dark coatings which make them look like concretions until they are broken. The profile is calcareous throughout, though lime concretions are absent from the C_1 horizon. On one side of the pit, partial involution of dark- and light-coloured soil materials has occurred at a depth of 3 ft. In a nearby second pit, cores of darker material, each about the size and shape of a former insect channel, extend down into the C_2 horizon. This profile represents a soil known locally as Morand II in the classification used for tax assessment.

3. Shallow Ragur soil from traprock—near buildings on Malegaon Farm (dry-farming research station), Sholapur, Bombay State.

a. Setting. This farm lies in a smooth, extensive plain which consists of broad gently rounded ridges separated by shallow valleys. Slopes are commonly long and gentle, with gradients below 5 per cent. and local relief is measurable in feet. The profile pit was on a very gentle slope of approximately 1 per cent. gradient. Most of the land is in cultivation, with sorghum appearing as the principal crop.

b. Profile description:

A_{1p} 0–9 in. Very dark greyish-brown (10 YR 3/2) clay which becomes very dark grey (10 YR 3/1) when it first begins to dry and then changes to dark grey (10 YR 4/1) when fully dry; very hard, friable, plastic, sticky; weak fine granular structure; few coarse to medium lime concretions.

A_{12} 9–18 in. Very dark greyish-brown (10 YR 3/2) clay which becomes very dark grey (10 YR 3/1) when it first starts to dry and then changes to dark grey (10 YR 4/1) when fully dry; very hard, friable, very plastic, very sticky; compound structure of moderate fine blocky peds with evident slick faces that crush readily to mixed weak and moderate medium granular peds; few coarse to medium lime concretions.

A_3 18–23 in. Very dark grey (10 YR 3/1) leaning towards very dark greyish-brown (10 YR 3/2) clay; very hard, friable, very plastic, very sticky; compound structure of strong medium to fine blocky peds that crush under considerable pressure to weak fine granular peds; slick faces are evident on the upper and lower surfaces of the blocky peds which are slightly elongated horizontally; few coarse lime concretions; lower boundary of the horizon varies up and down from approximately 20 to 26 in.

C_{ca} 23–30 in. The saprolite or well-weathered rock containing a marked accumulation of carbonate, especially in the upper part. Now largely loose, this seems a loam with a variegated colour pattern of yellowish-brown, pale brown, and light grey.

c. Additional notes. Effervescence is general throughout the profile but is strong only in the C_{ca} horizon, which is the upper part of the saprolite or murram. The calcium carbonate is finely disseminated, for the most part, though a few concretions are distributed through the solum. This profile represents Type A in the classification of Basu and Sirur (1938).

4. Deep Regur soil from limestone—about ¼ mile north-west of buildings on the Labhandi Experimental Farm, Raipur, Madhya Pradesh.

a. Setting. Known as the Chatisgarh plain, the region around Raipur is nearly level, with local relief measurable in inches. The broad level crests of the low ridges grade into long slopes leading down into very shallow valleys. The gradient of these long slopes is oftentimes as low as 1 or 2 per cent. The Regur soils occupy the shallow valleys and the lower portions of the long slopes. They are marked by gilgai micro-relief of low mounds and shallow depressions (5 to 15 ft. in diameter) and some termite mounds about 3 ft. tall. The soils on the ridge crests seem to be latosolic in character (on the basis of very few observations) and many of them are highly concretionary.

b. Profile description:

A_1 0–12 in. Very dark grey (5 Y 3/1) clay; extremely hard, very firm, very plastic, very sticky; weak medium granular structure; fine roots common as are fine black and brownish-black concretions.

A_3 12–28 in. Olive-grey (5 Y 4/2) to dark olive-grey 5 Y (3/2) clay; extremely hard, extremely firm, very plastic, very sticky; strong medium blocky peds that break down to weak fine and medium granular peds; faces of the blocky peds are commonly slick; fine roots common; few fine black concretions.

C_1 28–60 in. Olive-grey (5 Y 4/2) clay; extremely hard, extremely firm, very plastic, very sticky; strong medium to coarse blocky peds, most of which have slick faces; few fine black concretions and few fine roots; some variegation of olive-grey (5 Y 4/2) and olive (5 Y 4/3) colours make this layer seem brighter than the one immediately above.

C 60–80 in. Olive-grey (5 Y 4/2 to 5/2) clay with faint, fine, common mottles of light olive-brown (25 Y 5/4); almost massive in place but breaking into coarse very weak blocky peds; few roots; very coarse lime concretions (hard) and lime accretions (soft) are common.

c. Additional notes. All horizons of the profile are neutral to mildly alkaline in reaction, but lime concretions are absent above the C horizon. Fine plant roots are common in the A_1 and A_3 horizons, but the numbers drop off sharply in the C_1 horizon. From its appearance in the fields the soil seems extremely intractable and difficult to cultivate, except when it is used for paddy rice. The soil is badly infested with 'kans grass', probably because of the difficulties of tillage and consequent weed control. In the classification used in tax assessment for rural lands, this soil has the local name of Kanhar.

5. Deep Regur soil from alluvium—south-east of buildings on the Powarkheda Experimental Farm, 5 miles south of Hosangabad, Madhya Pradesh.

a. Setting. This is part of a nearly level landscape along the Narbada River, the northern boundary of the State. The surface is essentially level at the profile pit, and the local relief is generally measurable in inches. The level landscape, which parallels the river, seems to be a former flood plain. The experimental farm is about 5 miles south of the river channel and about as far north of the dissected margins of the Betul plateau. Low sandstone mountains lie north of the river in the state of Bhopal, and the same rock outcrops locally in a few low hills within the flood plain south of the river.

b. Profile description:

A_p 0–10 in. Dark greyish-brown (2·5 Y 4/2) heavy clay; hard, firm, very plastic, very sticky; weak medium granular peds; few medium black concretions; medium lime concretions common.

C_1 10–42 in. Dark olive-grey (5 Y 3/2) heavy clay which becomes olive-grey (5 Y 4/2) when crushed; very hard, firm, very plastic, very sticky; compound structure of moderate medium blocky peds which crush with difficulty to a mixture of moderate coarse granular and weak fine blocky peds; blocky peds have slick faces in the deeper part of the horizon; few medium lime concretions, few medium black concretions.

C 42–76 in. Dark olive-grey (5 Y 3/2) heavy clay which becomes olive-grey (5 Y 4/2 to 4/1) when crushed; hard, firm, very plastic, very sticky; compound structure of weak medium to coarse blocky peds that crush with moderate pressure to a mixture of weak medium granular and weak medium blocky peds; few medium lime concretions.

c. Additional notes. The alluvial nature of the sediments is indicated by the lenses and pockets of sandy clay loam and sandy clay in the sides of two of the four pits on the experimental farm and by the common occurrence of basalt and sandstone pebbles in the clay. Some of the pebbles also consist of unidentified rock species. In the bottom corner of one pit was a pocket of olive-grey (5 Y 4/2) clay containing many very coarse black concretions. A few roots extend the full depth of each pit, but numbers are small below the A_p horizon. In the classification for tax assessment, this soil is known as Mariyar.

6. Regur soil from colluvium—north of the buildings on the Rudrur Experimental Farm, about 15 miles south-west of Nizamabad, Hyderabad State.

a. Setting. The experimental farm lies in a broad plain with mixed relief, local differences in elevation being measurable in feet and in tens of feet. Low hills and ridges, usually tens of feet higher than the general level, rise above the plain in places as though they were erosional remnants. The site of the profile pit is the level floor of a valley or trough about 1½ miles wide between granitic ridges that rise some tens of feet above it. The regur soils commonly occur in these troughs or valleys and in other parts of the plain where the land surface is smooth or concave. They do not seem to run up on the slopes of the hills and ridges.

b. Profile description:

A_p 0–8 in. Dark greyish-brown (2·5 Y 4/2) clay; hard, friable to firm, plastic, sticky; weak fine to medium granular structure; few fine roots and few medium lime concretions, fine quartz pebbles common.

A_3 8–24 in. Dark greyish-brown (2·5 Y 4/2) to olive-grey (5 Y 4/3) clay; very hard, firm, very plastic, very sticky; almost massive in place but with very weak medium granular structure; few medium lime concretions and few quartz pebbles as well as some pockets of sand in this layer.

C_1 24–36 in. Olive-grey (5 Y 4/2) clay; very hard, very firm, very plastic, very sticky; weak coarse to medium blocky peds with slick faces which tend towards being platy in the lower part; some small pockets of sandy loam; few medium lime concretions and fine quartz pebbles.

c. Additional notes. This was No. 7 among the profiles studied by Desai (1942) and by Desai, Nagelschmidt, and Muir (1940). As noted in those earlier studies, the soil is mildly alkaline throughout, but contains lime concretions rather than finely divided calcium carbonate. Pockets of sandy material, discontinuous within the individual horizons, and a number of rock species in the form of pebbles indicate that the colluvium came from several sources. The general appearance of the valley or trough suggests that it may be an abandoned stream valley from some past geologic era.

Among the six profiles, the first one (No. 1) is thought to be representative of the main bodies of regur soils of India. Several other profiles examined are essentially like Profile No. 1 in the nature and sequence of horizons. Furthermore, it seems to be a central specimen with respect to

ranges in depth, texture, reaction, organic matter, and co-efficients of expansion and contraction, on the basis of the field studies, available laboratory data, and the discussions with Indian soil scientists. For these reasons it was selected as a type-specimen or norm for the group of regur soils.

The second and third profiles (Nos. 2 and 3) have thinner solums than does the first, but all three are considered to fall within the allowable range for a single great soil group. Profile No. 2, the solum of which is but slightly thinner than that of No. 1, may be a better type-specimen for the entire group of dark clay soils of tropical and warm-temperate zones, as is suggested later in this paper. It is believed by the author that Profile No. 3 is at or near the shallow end of the allowable range for the great soil group.

During field studies in Madhya Pradesh the author examined two profiles with solums consisting of rudimentary A horizons of brown (10 YR 4/3) clay loam, 6 to 12 in. thick. These soils may acquire typical regur profiles in time, but they now have much lighter-coloured A horizons lower in clay, lack the self-mulching properties, and differ from the typical regur soils in a number of ways. According to the approach in soil classification in the United States,[1] these shallow soils lie outside the limits of a great soil group typified by Profile No. 1 and would be considered lithosols.

The field observations of the author as well as the published descriptions (Tamhane, 1950; Wadia, 1945; Desai, 1942; Basu and Sirur, 1938) indicate that regur profiles derived from the traprock or basalt have a solum of moderate to shallow depth. Where the profiles, including the C horizon, are deep, the soils seem to have been formed at least in part from unconsolidated sediments or from some kind of rock other than basalt. Most of the regur soils considered to be many feet deep have apparently been formed from alluvium consisting chiefly of weathered basalt. Deep soils, including the C horizon as part of the profile, may also have been formed from limestone or perhaps from the shales mentioned by Hosking (1935). The last three profiles (Nos. 4, 5, and 6) described in this paper are examples of the 'deep' regur soils (Bal, 1935; Basu and Sirur, 1938; Tamhane, 1950). Positions in the landscape and the presence of several rock species among the pebbles in each profile indicate clearly that these soils were formed partly or entirely from alluvium. Among the regur soils considered to be deep, the whole soil mass seems to consist of alluvium or creep in many instances, whereas in others the solum seems to include both residual and transported materials. In the American scheme of classification, these deep soils represent intergrades toward the alluvial group. The most important properties are emphasized, however, if the soils are considered members of the regur group grading toward the alluvial group rather than as members of the latter.

Among the striking features of the regur soils, the low degree of horizonation is as prominent as are colour, texture, consistence, and

[1] A recent discussion of soil classification in the United States appeared in Soil Science, **67**, No. 2, 1949.

structure. The differentiation of horizons in the soils is extremely poor as compared to podzols, chestnut soils, grey-brown podzolic soils, and many other groups. It is true that the solum and the C horizon are set apart distinctly in regur soils derived from traprock. Moreover, the C_{ca} horizon is often clearly defined. In regurs from alluvium and in a profile from limestone (No. 4), however, the distinctions between the A and C horizons were obscure.

The lack of distinct horizons in regur profiles seems to be partly a reflection of the slowness with which horizon differentiation proceeds in fine-textured materials. It also seems to be partly due to the mixing of horizons which accompanies the alternate drying and wetting of the soils because of the seasonal distribution of rainfall. It has long been known that the formation of cracks as the soil dries after the end of the monsoon rains and the filling of those cracks when the next rains begin, together with the tremendous volume changes when the soils wet and dry, must result in much mixing of soil material, both vertically and horizontally. The importance of such volume changes is indicated by methods for construction of large buildings in Nagpur,[1] where foundation trenches are dug through the clay comprising the solum. The footings of foundations are set in the saprolite or murram in order to preclude cracking of a structure because of the shrinking and swelling of the clay.

The degree of mixing within the solum was indicated by the distribution of small pieces of red brick in an exposure of a typical regur soil from traprock at Nagpur. Trenches about 6 ft. deep had been dug for the pouring of concrete foundations for a building near the present city limits. Small pieces of red brick were distributed through the solum of the regur soil in the walls of the trenches, which were at least 200 ft. in length. This distribution of the pieces of brick was interpreted by the author as evidence of much mixing of soil materials within historic time. Evidence of much soil movement in Houston Black clay is given by Oakes and Thorp (1950). Taking a long-time view, it is possible to imagine the regur soils as churning slowly but steadily, a process certain to retard and perhaps even offset horizon differentiation.

The low degree of horizonation in the regur profiles leaves much room for difference of opinion as to proper identification and description of horizons. This also poses special problems in the classification of the soils.

Laboratory Data

It has been indicated in the preceding section that the regur soils are calcareous, mildly alkaline to neutral in reaction, high in clay and cation-exchange capacity, and low in organic matter. Numerous laboratory analyses are available, mainly for the surface soil (Bal, 1935; Hosking, 1935; Joshi, 1950), but some of the data are for entire profiles (Desai, 1942; Basu and Sirur, 1938; Raychaudhuri *et al.*, 1943; Roy and Das, 1952). In addition to published data the author had an opportunity

[1] Personal communication from R. J. Kalamkar.

to see some unpublished data at the Indian Agricultural Research Institute and the Nagpur Agricultural Research Institute. The profile data indicate that the soils are relatively uniform vertically. Values do not remain constant from top to bottom of the solum, but they tend to change little as compared to many other soil groups. This allows the extension of the analytical data from surface horizons to deeper parts of the solum with reasonable assurance that the errors thus introduced are small.

Soils of the regur group seem to be consistently alkaline in reaction, with the common pH range falling between 7·2 and 8·5 (Tamhane, 1950; Desai, 1942; Basu and Sirur, 1938; Roy and Das, 1952). Thus a relatively narrow range in pH covers most members of the group. Soils with higher pH values occur in some of the drier districts where exchangeable sodium tends to accumulate in the deeper profiles of lower-lying soils to make them more alkaline in reaction (Basu and Sirur, 1938).

Generally calcareous, the regur soils have a moderate range in content of calcium carbonate. This generalization is valid if the very shallow soils are excluded, some of which are high in carbonates. For the most part the regurs have carbonate contents ranging between 0·5 and 8·0 per cent. with extremes ranging from 0·1 to 20 per cent. (Tamhane, 1950; Desai, 1942; Basu and Sirur, 1938). The carbonates may be present as concretions distributed through the soil, as concretions that are concentrated in some part of the profile, in a finely divided state in all or some horizons, or in some combination of those forms. By and large, the soils with the least alkaline reactions contain black or brownish-black concretions that seem to be ferromanganiferous, which suggests that the soil material in those instances has been subjected to more weathering than is common. Among soils observed by the author, the regurs from alluvium, colluvium, and limestone contained the black or brownish-black concretions.

The regur soils are low in organic matter, apparently without exception. The low contents of organic matter, as compared to dark-coloured soils of temperate zones, have led to much question about the nature of the dark pigment (Harrison and Sivan, 1912; Joshi, 1950). There seems to be little need for postulating that the dark colour is due to substances other than organic matter, as a general rule. Contents of organic carbon in the A horizons of regur soils commonly range between 0·3 and 0·8 per cent., whereas those of nitrogen fall between 0·04 and 0·06 per cent. The amount of organic matter decreases slightly from top to bottom of the solum, but the change is small because the maximum content is itself small (Desai, 1942; Basu and Sirur, 1938; Raychaudhuri *et al.*, 1943; Roy and Das, 1952).

The average content of clay (less than 2 microns in diameter) in the regur soils is about 50 per cent., with the common range extending from 40 to 60 per cent. In some of the soils the clay contents are as high as 65 per cent. and in a few as low as 30 per cent. On the whole, however, the clustering of data around the average is striking. The available data for distribution of clay within the profile (Desai, 1942; Basu and Sirur, 1938; Raychaudhuri *et al.*, 1943; Roy and Das, 1952) indicate

that amounts tend to be uniform in the solum, except where there is evidence of stratification. Clay contents increase slightly with depth in some profiles, and the reverse is true in others. In the regur profiles derived from traprock there is a sharp change in clay content from the solum to the C horizon or saprolite (murram). All in all, regur soils are high in clay which is especially active, both chemically and physically.

Cation exchange capacities, on the average, are near 50 m.e./100 g. of soil, ranging mostly between 40 and 60 m.e./100 g. The exchange capacity seems to vary mainly with the content of clay, though it may change slightly with changes in amounts of organic matter. For the group as a whole, the variations in cation exchange capacity are small (Desai, 1942; Basu and Sirur, 1938; Raychaudhuri *et al.*, 1943; Roy and Das, 1952).

The high cation exchange capacities of regur soils are consistent with the identification of minerals of the montmorillonite group in the clay fraction of a Black Cotton soil from Hyderabad (Nagelschmidt, Desai, and Muir, 1940). Studied by Desai (1942) and by Nagelschmidt, Desai, and Muir (1940), the Black Cotton soil is described in this paper as Profile No. 6, a regur soil from colluvium. In subdividing the clay fraction, Desai (1942) found that 30 per cent. of the soil was below 0·06 micron in diameter and 10 per cent. between 0·06 and 0·1 micron. These two portions of the clay, comprising slightly less than half of the whole soil, were composed predominantly, if not entirely, of minerals of the montmorillonite group. Nagelschmidt, Desai, and Muir (1940) found kaolinitic minerals in the coarse clay fraction (0·1–2·0 microns), which comprised a small part of the total soil mass. Roy and Das (1952) report montmorillonite as the dominant clay mineral in a Black Cotton soil from Indore, although illite is also reported in appreciable quantities. Montmorillonitic clays are to be expected in soils with the high cation exchange capacities and the low contents of organic matter common to the regur soils. The plasticity and stickiness of the soils and their high coefficients of expansion and contraction are further evidence that the regurs are dominated by montmorillonitic clay minerals and contain small proportions of other kinds.

The laboratory data at hand for regur soils are in agreement with field observations that the changes within profiles are small. The data further emphasize the low degree of horizonation common to the soils as a group.

Relationships to Soils in the United States

The regur soils do not seem to be closely related to the chernozem and prairie soil groups of the United States, despite some features in common. The three groups are alike in the dark colour of the A horizon and in the importance of montmorillonitic clay minerals. The regurs differ from the other two groups, however, in the lack of an evident B horizon, in being calcareous throughout the solum, in the much lower contents of organic matter, in the more alkaline reaction of the A horizon, and in the very high coefficients of expansion and contraction. The marked swelling and shrinking of the regur soils with changes in moisture

content and the associated self-swallowing or self-mulching properties are lacking in chernozems and prairie soils. Thus the differences are many and important. Furthermore, comparison of the regur soils with other groups will demonstrate much closer kinship.

The regur soils are more closely related to the humic-gley group than to chernozems and prairie soils. Lack of good aeration with consequent dull colours is common to both regur and humic-gley soils, and the clay minerals in the two are similar. The humic-gley soils, however, are much higher in organic matter, commonly have distinct B horizons, range in reaction from strongly acid to mildly alkaline, and lack high coefficients of expansion and contraction. They do not exhibit the characteristic cracking and self-mulching properties of the regur soils. In fine-textured members of the humic-gley group, this can be ascribed to the fact that they do not become as dry as do the regur soils. In any event, the 'churning' of the soil associated with much drying, cracking, wetting, and swelling is absent in humic-gley soils. Thus the differences between typical members of the two groups are as large and important as the similarities. It does not therefore seem appropriate to consider them members of a single great soil group. At the same time, it should be recognized that the two groups grade into each other, both geographically and in definition.

Differences in concept of the rendzina group in Europe and in the United States have been pointed out by Oakes and Thorp (1950). The rendzinas of Europe seem to include soils that would be considered calcareous regosols or lithosols in the United States as well as soils that are intergrades between various azonal and intrazonal groups. The sequence of horizons, a mildly alkaline reaction, and a calcareous nature are the principal features that the European rendzinas, American rendzinas, and the regur soils have in common. The rendzinas in Europe typically lack the cracking and self-swallowing properties, are often stony, are commonly lower in clay, and have thinner horizons than do the regur soils and the American rendzinas. The similarities in profile seem less important than the differences between the European rendzinas, on the one hand, and the regur soils and American rendzinas on the other. Consequently, it does not seem appropriate to consider the regur soils of India and the rendzinas of Europe as members of a single great soil group, although it is felt that the American rendzinas and the regurs are. Because Houston Black clay and similar soils are different from rendzinas in Europe in many ways, the use of that name for them in the future seems improbable. At the same time, soils identical with European rendzinas occur in association with typical regur soils in India. The profiles considered to be calcareous lithosols by the author in India may be identical with some of the soils included in the rendzina group in Europe.

Oakes and Thorp (1950) have proposed that dark clay soils of tropical and warm-temperate zones, including the regurs of India, tirs of Morocco, black cotton soils in other parts of Africa, and some soils that were formerly called rendzinas in the United States, be recognized as a new great soil group. For this group they have proposed the name

'Grumusol', and have suggested Houston Black clay in Texas as a type-concept or norm. The properties listed to define the group apply well to the regur soils. Moreover, profile descriptions of regur soils and of Houston Black clay are further evidence of identity of the soils at the level of the great soil group. In the regur soils, as in Houston Black clay, there are no eluvial or illuvial horizons, the typical texture is clay, carbonates are generally present, the consistence is very plastic and sticky when the soil is wet, the colours are mainly dark ones of low chroma, the coefficients of expansion and contraction are high, and the contents of organic matter are low. The granular structure of the A horizon is less distinct in regur soils than in Houston Black clay, and the content of organic matter is slightly lower, as a rule. The gilgai microrelief of low knolls and shallow basins seems less common on the regur soils than on Houston Black clay, though the lack may reflect long-continued cultivation of the former. The author did not see prominent microrelief on the soils formed from basalt. Gilgai microrelief is as marked on the regur soils from limestone near Raipur, India, however, as it is on any soil in Texas. Careful comparisons of the morphological features and chemical characteristics make it clear that these soils represent a single great soil group occurring on separate continents. Furthermore, the group seems distinct from chernozems, prairie soils, and humic-gley soils, though further studies will be needed to define the margins between the dark clays of warm regions and the humic-gley group.

On the basis of the information available, it is suggested tentatively that the regur profile (No. 2) described near Betul, India, may serve as a norm for the profiles to be included in the group of dark clays. This one profile did not seem to be as typical for the large bodies of regur soils as did the profile (No. 1) at Alchapur and some of the others examined during the field studies. It does, however, seem to be a better abstraction of the profiles of the regur soils of India, on the one hand, and the former American rendzinas, on the other. It is very similar to though not identical with Houston Black clay, selected by Oakes and Thorp (1950) as type specimen for the proposed group of grumusols.

Available data leave little room for questioning the recognition of a separate great soil group of dark clay soils marked by self-swallowing properties. These occur chiefly in tropical and subtropical regions but extend into separate zones. The acceptance or rejection of the name 'Grumusol' suggested for this group by Oakes and Thorp (1950) lies in the future. Further study of the soils will also be needed to establish firmly a norm or central concept for the group as a whole. The validity of selecting the profile near Betul, India, as a norm for the group can only be determined through further investigations of the dark clay soils in various parts of the world.

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(*Received 31 July 1953*)

A STUDY OF THE BLACK COTTON SOILS WITH SPECIAL REFERENCE TO THEIR COLORATION

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THE black soils of the tropics and subtropics have been extensively studied in different parts of the world, and from the available evidence it appears that even on very differing parent materials, under certain soil-climatic conditions, some similar or common constituents are probably formed which impart dark or black colour to these soils. The investigations of Marchand (1924), Maufe (1928), Theron and Niekerk (1934), Hosking (1935), Basu and Sirur (1938), Nagelschmidt, Desai, and Muir (1942), Raychaudhuri, Sulaiman, and Bhuiyan (1943), del Villar (1944), Agarwal and Mukerji (1949), &c., throw considerable light on the physicochemical and mineralogical properties of these soils, but very little evidence seems to be available for explaining the causes for their dark or black coloration. Joshi (1950) is of the opinion that the black colour formation is an intrinsic property of the mineral clay which fixes the humus in a certain proportion to form the clay-humus complex which colours the soils black. It is of interest to mention here the concluding remarks of Joffe (1949) on the dark colour of these soils:

> In the discussion on the dark coloured soils of the tropics and subtropics the source of the black colour has been a kind of an enigma. At first, the colour was attributed to the organic matter, but when the facts demonstrated a low organic matter content of these soils, another explanation had to be provided. Del Villar is of the opinion that magnetite (Fe_3O_4) is responsible, in a large measure, for the dark colour. Raychaudhuri and associates are of the opinion that the dark colour is not due to the organic matter. Samples of dark coloured soil collected by the author in the Blida section of Algeria and in the Valley of Jezreel of Palestine remained dark after H_2O_2 treatment, but lost their colour and turned red upon ignition at 400–500° C.
>
> It might be that the dark coloured substances that persist after H_2O_2 treatment consist of humins and some type of bitumens. . . . These coal-like substances may cause a darkening of the soil when present in small quantities.

The organic carbon content of these soils, which have been referred to as tropical analogues of the chernozems, is very low and usually ranges from 0·4 to 0·8 per cent., whereas it is about 5 per cent. in the chernozems. The black colour of the chernozems could obviously be attributed to their high content of organic matter, but taking into consideration the very low content in the tropical black soils, it seems unreasonable to believe that organic matter alone can make them appear black. Hydrogen peroxide has been widely used as a mild reagent for destroying the organic matter in soils, and Raychaudhuri and co-workers (1943) and recently Joshi (1950) treated regur soils with this reagent to see whether the black colour was due to organic matter. They found that the dark colour persisted even after prolonged treatment. It was felt desirable, therefore, to

study in some detail the extent to which the colour and organic matter content of these soils were affected by hydrogen peroxide.

Soil samples were obtained from different parts of India with a view to including the more common black soil formations such as the 'Regur' of central and peninsular India, 'Kabar' of Bundelkhand, and the 'Karail' of the Gangetic alluvium. A brief description of these is given in Table 1. No well-marked horizon distinctions could be noticed in the profiles even up to a depth of 3 or 4 ft. in most examples, but the subsoils were distinctly more compact and dark as compared with the surface soils, and therefore the subsoils have generally been chosen for these studies. The Shahabad (Bihar) and Mirzapur (U.P.) soils are typical examples of the black soils, locally known as 'Karail', which were formed and are still being formed under waterlogged conditions prevailing for 4 or 5 months of the year (Kasinathan and Singh, 1952). It may be mentioned here that these are not the typical regur soils of the central and peninsular India, but as there are many physical and chemical characteristics common to both, it appeared interesting to have a comparative study of these with the regur soils whose formation is a subject of greater controversy. For comparative purposes a parallel study has also been made of certain of the red soils formed in the neighbourhood of the black soils.

TABLE 1

Soil Samples

Sample No.	*Locality (district) and Province*	*Depth*	*Parent material*	*Colour of the soil*•
6	Bheri (Shahabad), Bihar	2–3 ft.	Gangetic alluvium	Grey (5 Y 5/1; 5 Y 4/1 dk. grey, moist)
29	Chanwar (Mirzapur), U.P.	18–43 in.	,,	Dk. gr. brown (2·5 Y 4/2; 2·5 Y 3/2, v. dk. gr. brown, moist)
32	Karanpur (Mirzapur), U.P.	1½–13½ in.	Vindhyan Hills (mixed sandstone)	Strong brown (7·5 YR 5/6; 5 YR 4/4 reddish-brown, moist)
36	Churara (Jhansi), U.P. (Bundelkhand area)	30–48 in.	Gneiss and mixed sandstone	V. dk. gr. br. (2·5 Y 3/2; 10 YR 3/1 v.dk.gr. moist)
41	Nathi Khera (Jhansi), U.P. (Bundelkhand area)	30–51 in.	,,	Red (2·5 YR 4/6; 2·5 YR 3/6 dk. red, moist)
45	G.N. Palayam (Coimbatore), Madras	2–3 ft.	Granitic alluvium	Very dk. grey (2·5 Y 3/0; 10 YR 2/1 black, moist)
49	Kullioor (Coimbatore), Madras	2–3 ft.	Granite and gneiss	Dk. red (2·5 YR 3/6; 10 R 3/4 dusky red, moist)
52	Nagpur, Madhya Pradesh	10–39 in.	Traprock	Dk. gr. brown (2·5 Y 4/2; 2·5 Y 4/4 olive-brown moist)
55	Nagpur, Madhya Pradesh	0–7 in.	,,	Dk. brown (7·5 YR 4/4; 5 YR 3/3 dk. reddish-brown, moist)
64	Mathela (Khandwa), Madhya Pradesh	16–33 in.	,,	V. dk. brown (10 YR 2/2; moist also)
66	Mathela (Khandwa), Madhya Pradesh	0–5½ in.	,,	Dk. reddish-brown (5 YR 3/3 moist also)
69	Sakegaon (Bhusawal), Madhya Pradesh	12–28 in.	,,	Similar to 64

• *Munsell Soil Color Charts*, Hues—7·5 R through 5 Y

Experimental

In order to ensure an effective oxidation, a high concentration (40 vols.) of H_2O_2 was used in these experiments. It was found in the case of the black examples that, after a vigorous and almost instantaneous start, the reaction came almost to a stop within a few minutes and the colour of the soil remained unchanged. This behaviour of H_2O_2 was noticed only with the black soils; the reaction proceeded very smoothly with red soils. Determination of carbon content in the soils indicated that there was no loss of organic matter in the black soils whereas there was appreciable loss in the red soils. This suggests that the H_2O_2 was decomposed catalytically by the black soils. Whereas the red soils contain no carbonate and are invariably weakly acid, the black soils contain appreciable quantities of carbonate and usually have pH values above 7. It seemed possible that the difference in behaviour observed when the two soils are treated with peroxide might be due to these factors. To investigate the effect of a higher pH on the decomposition of the H_2O_2, the pH of a red soil was raised to 8, in one case by addition of sodium hydroxide solution and in a second experiment by addition of pure calcium carbonate. In the first case, the reaction with peroxide was no more vigorous than with the untreated soil. In the presence of calcium carbonate, however, it decomposed the H_2O_2 vigorously. The fine sand or silt fractions of many of these black and red soils also were found to decompose H_2O_2 in presence of $CaCO_3$, but such a reaction was not observed with their clay fractions. The fine sand or the silt fractions contain appreciable amounts of manganese compounds, whereas the clay-fractions contain comparatively very low amounts. Best (1931) found that in presence of manganese dioxide in alkaline solution, the hydrogen-peroxide is completely decomposed, while in acid solution, only sufficient reacts to reduce the manganese dioxide to the manganous condition. It thus appears that the MnO_2 of the calcareous black soils is responsible for the decomposition of H_2O_2. As mentioned earlier, this decomposition is not pronounced if the pH of the acid soil is raised to 8 by NaOH. The presence of $CaCO_3$ at this pH probably keeps a greater proportion of the manganese compound in an active state; the actual mechanism of the reaction, however, is not clear.

McLean (1931) and Hosking (1932) showed that the oxidation of the organic matter by H_2O_2 is not complete in calcareous soils. Hosking (1932) working on the heavy black basaltic soils of Australia found that complete oxidation took place if the soil was first acidified to remove calcium carbonate and that the soil so oxidized turned light grey or brown. Joshi (1950) working on some black soils of Madhya Pradesh (India) found that the soils did not lose their colour by a similar treatment. The soils under present study were investigated in a similar manner. The carbonates were decomposed by addition of a calculated amount of dilute hydrochloric acid. It was found that unless the soils were brought to as low a pH as 3, the carbonates were not completely decomposed. These carbonate-free soils on treatment with H_2O_2 lost their basic dark colour completely (Table 2). It may be seen that the

decolorization is more clearly marked when the soils are moist. Some of the samples which are light yellow-brown or reddish-yellow when moist appear olive-grey or dark brown in the dry state and this possibly is due to the presence of the small quantities of MnO_2 or Fe_2O_3 in such samples. The very fact that the colour of these peroxidized soils lightens when they are moist, instead of becoming darker as in normal soils, indicates that these soils lose their basic dark colour completely.

TABLE 2

Colour of the Carbonate Free Soils after H_2O_2 Treatment

Sample No.	*District*	*Colour*
6	Shahabad	Light olive-grey (5 Y 6/2; 5 Y 8/3 pale yellow, moist)
29	Mirzapur	Grey brown (2·5 Y 5/2; 2·5 Y 7/4 pale yellow, moist)
36	Jhansi	Light grey-brown (2·5 Y 6/2, 10 YR 6/4 light yellow-brown, moist)
45	Coimbatore	Dk. grey (10 YR 4/1; 5 Y 7/3 pale yellow, moist)
52	Nagpur	Dk. grey-brown (10 YR 3/2–3/3; 7·5 YR 6/6, reddish-yellow, moist)
64	Khandwa	Brown to dk. brown (7·5 YR 4/2; 7·5 YR 6/6 reddish-yellow, moist)

Amount and Nature of, and the effect of Hydrogen Peroxide on, the Organic Matter present in the Black and Red Soils

The carbon in these soils was determined by a semi-micro combustion method (Rickson, 1948). For nitrogen, Bal's (1925) wet digestion method was employed and aliquots were steam distilled in the Markham's (1942) apparatus. As is evident from Table 3, some of the red soils contain more organic carbon than their adjoining black soils and it was found that after removing the free oxides of iron (which might have a masking effect on the basic colour of the red examples) the residues obtained were not dark coloured. This fact indicates that it is not only the amount but the nature of the organic matter which is responsible for the dark colour of the black soils. The black soils invariably have a higher C/N ratio than do the red ones. This difference is not always pronounced in the surface soils. For such comparisons it is more reasonable to take the subsoils which suffer temporary interferences to a lesser degree. In the U.P. and Bihar samples (6, 29, 32, 36, and 41) which have been formed in a more humid climate, this difference is less conspicuous.

It was felt that determination of the residual carbon and nitrogen in the peroxidized soils would help to characterize the types of humus present in these soils. It appears from the figures (Table 3) that for the same amount of H_2O_2 the organic carbon of the red soils is less resistant to the action of H_2O_2 than that of the black examples, but, as will be seen later, there are other factors which are responsible for the higher resistant-carbon contents of the latter type. The nitrogenous compounds in all these cases seem to be very resistant as practically no loss of the element is caused by H_2O_2 oxidation. McLean (1931) found that above a certain stage of oxidation there is no further attack on the nitrogenous

compounds of the organic matter in soils. In these tropical soils perhaps the nitrogen is already in this state, and, therefore, there is very little loss of this element by H_2O_2 oxidation.

TABLE 3

C and N in the Black and Red Soils

Sample No.	*Before* H_2O_2 *treatment*			*After* H_2O_2 *treatment*			
	C %	N %	C/N	C %	N %	C/N	$\frac{R.C.}{T.C.} \times 100$*
6 Black	0·47	0·069	6·81	0·19	0·065	2·92	40·42
29 Black	0·51	0·074	6·89	0·23	0·054	4·26	45·1
32 Red	0·32	0·057	5·61	0·08	0·057	1·40	25·00
36 Black	0·45	0·055	8·18	0·17	0·054	3·15	37·77
41 Red	0·13	0·029	4·48	0·04	0·022	1·82	30·77
45 Black	0·80	0·047	17·02	0·33	0·045	7·33	41·25
49 Red	0·30	0·049	6·12	0·10	0·045	2·22	33·33
52 Black	0·54	0·042	12·86	0·24	0·038	6·32	44·44
55 Red	0·76	0·083	9·15	0·27	0·082	3·29	35·52
64 Black	0·86	0·063	13·65	0·32	0·056	5·71	37·21
66 Brown	0·35	0·042	8·33	0·10	0·036	2·78	28·57

*R.C. = Resistant carbon.
T.C. = Total carbon.

Effect of Exchangeable Bases on the Amount of Organic Matter oxidized

In some qualitative experiments it seemed that the efficiency of the H_2O_2 in oxidizing the humus of a soil might also depend upon the exchangeable bases. Hosking (1932) working on a range of soils came to the conclusion that the decomposition of the organic matter of a soil by means of hydrogen peroxide is a function of the hydrogen-ion concentration of the soil. His results suggest that a portion of the organic matter is oxidized irrespective of the soil reaction, while the oxidation of the remainder is a definite function of the hydrogen-ion concentration, the relation being expressed by the equation

$$\log\left(\frac{x}{100-x}\right) = K(\mathrm{pH}-\mathrm{pH}_1)$$

where x is the proportion of oxidizable organic matter destroyed at any given pH value and $\mathrm{pH}_1 = 7{\cdot}87$ (reaction value for 50 per cent. oxidation), and $K = 0{\cdot}673$.

No mention of the exchangeable bases in the above equation has been made. In his studies Hosking prepared different samples of a H-soil at different pH values by using $Ca(OH)_2$. Thus the exchangeable bases in his samples were (more or less) mostly H and Ca. It was felt that if any other base in place of Ca is taken as the exchangeable base, the amount of organic matter decomposed at the same pH would probably be different. After removing the $CaCO_3$ from a black cotton soil, one portion was saturated with NaCl and the other with $CaCl_2$. The pH of the soils was then brought to 7 by adding dilute NaOH solution in both the cases. $Ca(OH)_3$ was not used in the case of the Ca-saturated sample to

avoid the formation of $CaCO_3$ in presence of which, as mentioned earlier, the H_2O_2 is catalytically decomposed. Taking into consideration the relative stability of the exchangeable calcium to removal by sodium, particularly when the amount of NaOH used was very small, it was felt that the exchangeable-base status of the Ca-saturated soil would not be appreciably affected.

The calcium and sodium soils were treated with equal volumes of H_2O_2 also adjusted to pH7. The pH of the reaction mixture was checked during the course of the reaction and, where necessary, the pH was brought to 7. It was found that the Na-soil lost its dark colour almost completely whereas the Ca-soil, with the same amount of H_2O_2, did not. It may be seen from the carbon figures (Table 4) that the carbon of the

TABLE 4

C and N in Calcium- and Sodium-saturated Soils

	Per cent.				
	Before H_2O_2 *treatment*		*After* H_2O_2 *treatment*		
Soil	C	N	C	N	$\frac{R.C.}{T.C.} \times 100$
Ca-soil .	0·72	0·051	0·44	0·047	61·11
Na-soil .	0·74	0·049	0·22	0·045	29·73

Ca-soil is much more resistant than that of the Na-soil. On substituting these figures in Hosking's equation, different values for *K* are obtained if the exchangeable bases are ignored. Thus the amount of organic matter oxidized by H_2O_2 is not only a function of the hydrogen-ion concentration but also of the exchangeable bases present at that pH. One obvious explanation of this seems to be the degree of dispersion of the clay-humus complex, more dispersed material providing greater surface area for the effective oxidation by H_2O_2. Besides this, the closed-chain organic compounds of calcium would probably be more resistant than the open-chain compounds of the monovalent bases.

Considering the action of H_2O_2 on the black and red soils, it thus appears that the greater resistance of the organic carbon in the black soils might be partly due to their Ca-saturation; the higher values obtained for resistant carbon do not, therefore, necessarily reflect a difference in the nature of the organic matter of the two soil types. In order to investigate this point, the behaviour of the two soils when saturated with the same base was studied. Saturation with calcium was found more convenient because sodium disperses the soils so much that the washing of the soils becomes difficult. Further, it was felt that the organic matter present in the whole soil may also contain non-humified materials and the organic matter associated with the clay fraction would be a better representative of the true humus. In addition to this, it was found that only the clay fractions of these soils, particularly of the black examples, very closely resemble in colour their corresponding soils (Tables 1 and 5). The silts, fine- and coarse-sand fractions bear little resemblance to their

soils and in many cases are almost colourless. These observations are in conformity with the findings of Joshi (1950). Taking these facts into consideration, it was considered more reasonable to study the action of H_2O_2 on the clays at the same pH and having almost the same degree of base saturation.

For the clay separation the soils were first dispersed by 'calgon' and then separated from the other fractions by repeated sedimentation. The clay suspensions were flocculated with $CaCl_2$ solution added in quantity just enough to bring about the flocculation, washed free of the chlorides, centrifuged, and dried. Equal weights of these oven-dried clays were treated with equal volumes of hydrogen peroxide. The colours of these clays, before and after the H_2O_2 treatment, are given in Table 5. It may be observed that the decolorization is more distinct in the clays, especially of the black ones, than it is in some soils.

TABLE 5

Colour of the Clays

Sample No.	*Before* H_2O_2 *treatment*	*After* H_2O_2 *treatment*
6 Black	Dk. grey (5 Y 4/1; 5 Y 4/1 moist)	Pale olive (5 Y 6/4; 5 Y 6/4 moist)
29 Black	Dk. gr. brown (2·5 Y 4/2; 2·5 Y 4/2 moist)	Strong brown (7·5 YR 5/6; 10 YR 5/4 yellowish-brown, moist)
32 Red	Reddish-brown (5 YR 4/3; 5 YR 3/3, dk. reddish-brown, moist)	Red (2·5 YR 4/8; 2·5 YR 4/8 moist)
36 Black	V. dk. grey (5 Y 3/1; 5 Y 3/1 moist)	Brownish-yellow (10 YR 6/6; 2·5 Y 6/4 light yellowish-brown, moist)
41 Red	Red (2·5 YR 4/6; 2·5 YR 3/6 dk. red, moist)	Dk. red (2·5 YR 3/6; 2·5 YR 4/8 red, moist)
45 Black	V. dk. grey (10 YR 3/1; 10 YR 3/1 v. dk. grey, moist)	Lt. brown grey (2·5 Y 6/2; 2·5 Y 6/2 moist)
49 Red	Dk. reddish-brown (2·5 YR 3/4; 2·5 YR 3/4, moist)	Dk. red (10 R 3/6; 10 R 3/6 moist)
64 Black	Dk. grey (10 YR 4/1; 10 YR 3/2 v. dk. greyish-brown, moist)	Yellow-red (5 YR 4/8; 5 YR 5/8 moist)
66 Brown	Dusky red (5 YR 3/3; 5 YR 3/4 dusky red, moist)	Dk. reddish-brown (2·5 YR 3/4; 2·5 YR 3/6 dk. red, moist)
69 Black	Similar to 64	Brown (7·5 YR 5/4; 7·5 YR 6/6 reddish-yellow, moist)

The traces of the very light greyish tinge in such peroxidized soils are thus obviously due to the coarser fractions containing grey or black particles of resistant oxides of iron or manganese. This is confirmed by the fact that a dried mixture of these peroxidized clays with their fine sand fractions added in the same proportion as in the original soils gives a similar light greyish tinge.

In Table 6 the figures for carbon, nitrogen, and C/N ratio of these clays before and after H_2O_2 treatment are given. It is evident from these figures that the clays from the red soils invariably contain more nitrogen. The carbon figures are variable. Some of the red clays contain higher carbon than their corresponding black examples, whereas in others they contain more or less the same amount and so the C/N ratios of the black

clays are invariably higher. These ratios are rather variable in the peroxidized clays. Similar to the soils, nitrogenous compounds of all the clays are very resistant and so the C/N ratios have become very low after peroxidation. The most remarkable differences are indicated in the C/N ratios of the organic matter oxidized, those from the black examples being much higher. The percentages of the resistant carbon in the black examples are invariably lower than their corresponding red examples. It may be recalled that these resistant carbon figures were higher in the case of the peroxidized black soils. Thus, it is evident that the humus of the black clays, having almost the same degree of base saturation, is less resistant to the action of H_2O_2 than those of their red examples.

TABLE 6
C *and* N *in the Clays*

Sample No.	*Before* H_2O_2 *treatment*			*After* H_2O_2 *treatment*				
	C %	N %	C/N	C %	N %	C/N	$\frac{(T.C.-R.C.)^*}{(T.N.-R.N.)}$	$\frac{R.C.}{T.C.} \times 100$
6 Black	0·62	0·085	7·29	0·13	0·076	1·71	54·44	20·97
28 Black	0·64	0·091	7·03	0·12	0·081	1·48	52·0	18·75
32 Red	0·91	0·140	6·50	0·21	0·121	1·74	36·84	23·08
35 Black	0·82	0·102	8·04	0·13	0·098	1·33	172·5	15·85
40 Red	0·58	0·137	4·23	0·21	0·118	1·78	19·47	36·20
45 Black	0·67	0·057	11·75	0·17	0·048	3·54	55·55	25·37
49 Red	0·55	0·104	5·29	0·20	0·095	2·11	38·89	36·36
64 Black	0·94	0·061	15·41	0·21	0·058	3·62	243·3	22·34
66 Brown	0·96	0·099	9·70	0·23	0·066	3·48	22·12	23·96
68 Black	0·76	0·069	11·01	0·16	0·065	2·46	150·0	21·05

* i.e. C/N of the organic matter oxidized.

This lower resistance is not indicated in the original black soils probably because of their base saturated nature as against the base unsaturated nature of the red soils.

Discussion

Raychaudhuri and co-workers (1943) and Joshi (1950) treated regur soils with H_2O_2 with a view to seeing whether the dark colour is due to organic matter and found that it persists even after prolonged treatment. In the present studies it has been found that a fairly concentrated solution (20 to 40 vols.) of this reagent, if taken in sufficient quantity, can completely remove the basic dark colour of these soils provided the carbonate is first removed. This decolorizing effect is more clearly indicated if the clay fractions, which are very similar to their original soils, are treated with this reagent. The role of organic matter in this change of colour seems to be very definite in view of the fact that by increasing the amount of H_2O_2 slightly decolorized to completely decolorized products are obtained with diminishing contents of carbon. the latter having lost practically all their carbon. This greater decolorization with a greater loss of carbon shows a very close association of the dark colour of these soils with their organic matter.

The total amount of carbon in the black and adjoining red soils or their clays is not remarkably different and is below 1 per cent. in all cases. Some difference is indicated in their C/N ratios, those of the black examples being somewhat higher than their corresponding red examples, but much importance cannot be attached to such ratios because the total carbon and nitrogen contents do not necessarily reflect the actual amount of those organic compounds which are responsible for the dark colour. The clays of the black soils lose much more carbon when treated with H_2O_2 than do those of the red examples. This indicates that the organic matter of the black soils has undergone a greater degree of humification (Robinson and Jones, 1925). Hydrogen peroxide can dissolve the whole of the lignin of the humus (Shrikhande, 1947). Thus the lower resistant carbon figures in the black soil clays would indicate that their lignin content is comparatively higher than those of the red clays.

So far as the black and red colours of these soils are concerned, it must be emphasized that, in addition to the dark organic substances, the nature and amount of clays present in the two types are equally important factors. The black soils contain usually 40 to 60 per cent. clay which is mostly of the montmorillonite type, whereas the red soils contain a much lower percentage of clay which is mostly of kaolinitic type richer in oxides of iron. Dispersion over the very large surface of the montmorillonitic clays of the black soils would enhance the effectiveness of the organic matter in colouring the soil. Presumably the low content of the dark organic matter of the red soils coupled with their lower surface areas allow the iron oxides to dominate the colour. Some of the essential conditions and also the role of the clays in the formation of the dark clay humus complex will be dealt with separately.

The black soils under study represent three sub-types—'Regur' of central and peninsular India, 'Kabar' of Bundelkhand area, and 'Karail' of the Gangetic alluvium. Their organic matter behaves similarly when oxidized with H_2O_2, thus suggesting a similar mode of formation. The 'Karail' soils are submerged under water for a portion of the year and are formed under conditions somewhat similar to the Vlei soils. It thus appears probable that the regur and Kabar soils also might have been formed under some type of intermittent anaerobic conditions.

Summary

A study of the dark colour of some Indian black soils has been made by oxidation with H_2O_2. The calcareous soils containing even traces of MnO_2 decompose the H_2O_2 and their colours remain almost unchanged; but after a pretreatment of these soils with dilute hydrochloric acid to decompose the carbonates, their basic dark colours are completely decolorized by H_2O_2. The reasons for the dark colour associated with the organic matter so oxidized have been discussed.

Although the organic carbon of the black soils appears more resistant to the H_2O_2 oxidation as compared with the carbon of the adjoining red soils, it has been shown that this apparent resistance is due to their

Ca-saturation. The clay fractions, which are very similar in colour to their original soils, contain less H_2O_2 resistant organic carbon than their adjoining red examples. The nitrogen of all these soils is very resistant to this reagent.

The regur or black cotton soils of central and peninsular India or the 'Kabar' soils of Bundelkhand contain organic matter which behave similarly on H_2O_2 oxidation to that of the 'Karail' soils of the Gangetic alluvium, thus giving an indication of their formation under somewhat similar intermittent anaerobic conditions.

Acknowledgement

The author wishes to express his gratitude to Sir William G. Ogg for his permission to undertake this work at Rothamsted Experimental Station. Acknowledgement is due to Dr. A. Muir for his helpful criticism and encouragement during the progress of the work and to Dr. C. Bloomfield for his valuable suggestions.

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(Received 6 June 1953)

SALINE AND ALKALI SOILS OF THE INDIAN GANGETIC ALLUVIUM IN UTTAR PRADESH

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In the Indian Gangetic alluvium of Uttar Pradesh where the intensity of cultivation is very heavy an appreciable fraction of the land is seriously affected by the presence of salts. The saline and alkali lands of the State of Uttar Pradesh are collectively known by the local name of *usar* lands. It has been estimated that about 2·1 million acres of land in this state are lying uncultivated due to the presence of alkali in some form, and their reclamation is a matter of considerable economic importance. A much larger portion of the cultivated area contains soils that are only mildly saline or alkaline and are not yet totally unfit for cultivation, but on which crop yields are low and agricultural production unprofitable. The concentration of saline and alkali soils is found to be maximum in the more arid central and north-western portions of the State and in the districts on the left bank of the River Ganges.

Analytical data in respect of saline and alkali soils of the Indian Gangetic alluvium are extremely meagre. Some work has been in progress on such soils in these laboratories since 1936. A few isolated data in respect of cultivated saline and alkali soils of the Gangetic alluvium in Unao District were reported by Mukerji, Agarwal, and Mukerji (1946) and of Hardoi District by Mukerji and Agarwal (1947). Similarly, saline soils of the Gangetic riverain tracts at Hastinapur have recently been described by Agarwal and Mehrotra (1952). However, the data so far available have proved inadequate since they do not give a complete picture of the status of soil salinity or alkalinity in so far as it affects the management or improvement of these soils. The appraisal of soil salinity and its application to practical agriculture in the methods of the management and reclamation of such soils have been completely reoriented in recent years as a result of work conducted at the U.S. Regional Salinity Laboratory, Riverside, California. Scofield (1941) was the first to suggest that the concentration and nature of salts in the soils at the field moisture content were the main factors responsible for adverse effects on plant-soil-water relationships. This concept has since been worked up in considerable detail in America to appraise the salinity status of soils as it may affect plant life. For this purpose the concentration of salts in the saturation extracts of the soils and the composition of the saturation extracts are being utilized by soil workers in all work on saline and alkali soils. Since data on the saline and alkali soils of the Indian Gangetic alluvium on these lines are not available, an attempt has been made in this paper to present analytical data on these lines for some of the more common types of such soils found in Uttar Pradesh with a view to appraising their salinity status *vis-à-vis* the possibility of their reclamation.

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Methods and Technique of Work

Samples of soils from profiles representing typical saline and alkali soils of the Gangetic alluvium were collected from the districts of Lucknow and Hardoi in Uttar Pradesh. These sites represent areas that were previously uncultivated, but are now under reclamation by the Uttar Pradesh Department of Agriculture. For the sake of comparison some soil profiles from the cultivated areas of the adjoining district of Kanpur in tracts where soil salinity is slowly becoming a problem were also included in these studies. The methods of analysis used were those recommended by the U.S. Regional Salinity Laboratory (1947). Insoluble carbonate was assessed by observing the degree of effervescence with dilute HCl. pH values were determined by means of a glass electrode and a Macbeth pH meter at 1:2·5 and 1:10 soil-water ratios. Saturation percentage was estimated by stirring the soil after adding water from a burette till saturation was attained. Saturation extracts were prepared from a Houston filter pump by using a tyre pump and the values for the electrical conductivity were found on a Philips conductivity apparatus. Soluble-sodium concentration in saturation extracts was determined by the uranyl-zinc-acetate method. Gypsum content and exchange capacity were determined by the ordinary methods of extraction with ammonium acetate. The usual macro methods were adopted for determining the composition of the saturation extracts from the surface soils.

Description and Characteristics of the Soils

In order to have a clear picture of the salinity status of the soils as they behave in the field, samples from complete profiles were taken. Table 1 contains the descriptions of the profiles. Six profiles were sampled from uncultivated areas in the districts of Lucknow and Hardoi and three from cultivated lands in the district of Kanpur. Profile 1 was obtained from a site in the uncultivated saline and alkali area which had a fairly good natural vegetation. Although the surface soil rested on heavier calcareous subsoils, the internal drainage was only slightly impeded and permeability seemed to be good in the surface layers. Profile 2 represents the area which had very little drainage, and salt efflorescence on the surface was fairly widespread. Profiles 3 and 4 were sampled from typical alkali lands in which the internal drainage was greatly restricted by the presence as pans in subsoils of hard indurated $CaCO_3$ nodules cemented together. Profile 5 is a typical example of clayey alkali land with heavier clay-pan subsoils and in which the surface calcareous soils lie on permanently wet sub-soils with restricted drainage. In Profile 6 the presence of a *kankar* ($CaCO_3$ nodules) pan renders internal drainage difficult. For cultivated lands, the three profiles represent the three stages in internal drainage. The first profile is non-calcareous, and the second profile shows only mild calcareousness in the bottom, but the third profile is calcareous throughout. Such topographic effects have been found in the whole of the Gangetic alluvium (Agarwal and Mukerji 1951).

TABLE 1

Description of the Soils used in the Study

Profile No.	*Lab. No.*	*Depth (in.)*	*Locality*	*Description*
			(Uncultivated land)	
1	C–1992	0–18	Kasimabad (Hardoi)	Grey; sandy loam; friable; drainage good; calcareous
	C–1993	18–27		
	C–1994	27–48		Brown-grey; clay loam; calcareous; drainage slightly restricted
	C–1995	48–72		Brown-grey soil; loam; calcareous; water-logged
2	C–1942	0–12	Kasimabad (Hardoi)	Brown; light loam; friable; calcareous with salt efflorescence
	C–1943	12–30		Brown with iron mottlings; clay loam; lime deposits visible
	C–1944	30–42		
	C–1945	42–72		Dark brown; clay loam; highly alkaline
3	C–753	0–12	Malihabad (Lucknow)	Grey-brown; loam; calcareous with restricted drainage
	C–754	12–27		Brown; clay loam; iron mottling; restricted drainage
	C–755	27–48		Brownish-yellow; clay loam; no drainage; deposits of lime nodules
	C–756	48–58		
4	C–2238	0–18	Kasimabad (Hardoi)	Grey-brown; loam; slightly permeable; mildly calcareous
	C–2239	18–30		Yellowish-brown; clay loam; mildly calcareous
	C–2240	30–42		Dark yellowish-brown; clay loam; lime deposits on the bottom
5	C–1865	0–10	Kasimabad (Hardoi)	Grey; clay loam; friable; calcareous; with salt deposits on the surface
	C–1866	10–22		Brown; clay loam; indurated; drainage restricted
	C–1867	22–42		Dark brown; clay; iron mottlings; compact and waterlogged; mildly calcareous
	C–1868	42–60		
6	C–2067	0–9	Kasimabad (Hardoi)	Brown; loam; slightly friable; mildly calcareous
	C–2068	9–21		
	C–2069	21–33		Dark brown; clay loam; semi-indurated; nodules of lime deposits in the bottom
	C–2070	33–72		
			(Cultivated land)	
7	C–33	0–12	Ghatampur (Kanpur)	Dark grey; clay loam; non-calcareous; drainage good
	C–34	12–24		
	C–35	24–36		Grey; clay loam; slightly compact; non-calcareous; drainage good
	C–36	36–48		
8	C–2893	0–12	Derapur (Kanpur)	Dark grey; clay loam; friable; non-calcareous; neutral in reaction
	C–2894	12–24		
	C–2895	24–36		
	C–2896	36–48		Grey; clay; compact; small lime nodules; drainage slightly restricted
9	C–231	0–12	Maswanpur (Kanpur)	Light grey; sandy loam; calcareous; alkaline
	C–232	12–24		Light grey; clay loam; slightly indurated; calcareous; alkaline
	C–233	24–36		Grey; clay loam; lime deposits; drainage restricted
	C–234	36–48		

Salinity Appraisal

Results of chemical analyses of the soils from the typical profiles described above are given in Table 2 and those for the saturation extracts of the surface soils in Table 3.

Profile 1 can be classed as a soil approaching the normal arid type of the locality, although the pH values in all the four layers are high. It is more calcareous in the bottom layers. The texture appears to be heavier in the subsoils than in the surface soils. The conductivity of the saturation extracts is less than 1·5, but the soluble-sodium percentage in the saturation extracts is high, reaching a value of 86 per cent. in the third layer. Calcium is not the chief soluble cation in the saturation extracts of the soils of all the layers of this profile. In the surface layer (Table 3) it is present to the extent of only 30 per cent. The soils represented by this profile appear at present to be normal in regard to their general effect on plant growth in the field, but they contain enough soluble sodium which may ultimately render them alkaline if the concentration of total soluble salts in the profile is allowed to increase further as a result of cultural practices.

Profile 2 may be taken as an example of a saline-alkali soil since the conductivity of the saturation extracts is more than 4 millimhos/cm. and the exchangeable-sodium percentage is more than 15. Only the clayey fourth layer seems to approach the limits for a normal soil. The profile contains maximum insoluble $CaCO_3$ at the surface. All the four layers of the profile have high pH values. The sodium concentration of the saturation extracts of the first three layers is very high, and for this reason carbonates come out to be the predominating anions in the extract. Gypsum is present only in traces rendering further addition of this amendment necessary if reclamation through leaching is desired.

Profile 3 is yet another example of saline-alkali soil, but in this case maximum calcareousness is found in the bottom and gypsum, even in traces, is absent from the lower layers. The saturation extracts contain predominantly sodium and carbonates ions. Profile 4, which also shows the characteristics of a saline-alkali soil, does not contain as much soluble salts as contained in Profiles 2 or 3; and the percentage exchangeable sodium is also low in comparison. Profiles 3 and 4 have developed under very restricted drainage as a result of the presence of indurated pans of $CaCO_3$ nodules in the subsoils.

Examples of non-saline-alkali soils are afforded by Profiles 5 and 6. Both are calcareous with very high pH values. The conductivity of the saturation extracts is less than 4 millimhos/cm., but the exchangeable-sodium percentage is, in four of the eight samples, more than 15. The last two layers of Profile 5 and the last layer of Profile 6, however, show lower exchangeable-sodium contents. The drainage in both these profiles is restricted, due to the presence of a clay-pan in the subsoils of the former and a $CaCO_3$ pan in the sub-soil of the latter.

The profiles from the cultivated areas show varying degrees of salinity and alkali. Whereas Profiles 7 and 8 reveal the usual features of normal cultivated land with no salinity or alkali, the data from Profile 9 suggest

TABLE 2

Analysis of Saline and Alkali Soils from Indian Gangetic Alluvium.
Soil Determinations

Profile No.	Lab. No.	Depth (in.)	Insoluble CO_3 test	pH		Saturation (%)	Saturation extract			Exchange capacity (m.e. %)	Exchangeable Na (%)	Gypsum	Remarks
				1 : 2·5	1 : 10		Conductivity (millimhos/cm.)	Soluble Na m.e./litre	% soluble Na				
1	C–1992	0–18	0	9·55	8·80	37·2	1·010	5·1	50·5	6·24	3·2	nil	N
	C–1993	18–27	+ +	9·80	9·30	49·0	1·377	8·7	63·0	9·68	5·1	nil	N
	C–1994	27–48	+ +	9·30	9·05	66·0	1·082	9·3	86·1	7·04	9·2	nil	N
	C–1995	48–72	+ + +	9·40	8·95	47·3	1·010	7·5	74·3	5·20	6·6	nil	N
2	C–1942	0–12	+ + +	11·05	10·85	35·4	13·528	145·3	100·0	7·92	70·0	traces	SA
	C–1943	12–30	+	10·95	10·60	37·6	11·837	116·1	98·1	9·44	70·0	traces	SA
	C–1944	30–42	+	10·80	10·75	41·8	4·590	34·6	75·4	10·00	15·0	traces	SA
	C–1945	42–72	+	10·10	10·10	52·6	2·805	13·9	49·5	7·68	6·0	traces	N
3	C–753	0–12	+ +	11·50	11·30	43·4	16·834	155·9	92·6	13·28	45·0	traces	SA
	C–754	12–27	+	11·40	11·20	38·4	13·774	129·4	94·0	10·32	45·0	nil	SA
	C–755	27–48	+ +	11·20	11·05	40·0	15·782	154·1	97·7	13·36	60·0	nil	SA
	C–756	48–58	+ + +	10·80	10·80	44·3	13·061	126·1	96·6	11·92	43·0	nil	SA
4	C–2238	0–18	+	11·20	11·10	34·0	5·611	48·8	87·0	8·40	23·0	nil	SA
	C–2239	18–30	+	11·10	10·95	43·8	8·417	78·5	93·2	11·60	35·0	nil	SA
	C–2240	30–42	+ +	10·80	10·90	51·2	4·887	46·8	95·7	13·44	33·0	nil	SA
5	C–1865	0–10	+ + +	10·45	10·35	35·0	2·913	21·9	75·3	8·80	15·0	nil	NSA
	C–1866	10–22	+ +	10·90	11·00	69·2	2·913	23·5	80·8	9·60	17·0	nil	NSA
	C–1867	22–42	+	10·10	10·60	87·8	1·894	11·1	58·7	8·80	8·0	traces	N
	C–1868	42–60	+	9·80	10·00	81·0	1·082	7·8	72·2	7·10	7·0	traces	N
6	C–2067	0–9	+	10·90	11·20	38·7	2·913	27·1	93·1	10·00	23·0	nil	NSA
	C–2068	9–21	+	11·20	11·20	49·8	1·377	10·7	77·5	11·76	12·0	nil	NSA
	C–2069	21–33	+ + +	10·80	10·90	58·0	2·525	23·5	92·9	8·40	21·0	nil	NSA
	C–2070	33–72	+ + +	9·90	9·85	47·1	1·761	14·2	80·7	5·84	13·0	nil	NSA
7	C–33	0–12	0	6·30	6·50	43·8	1·946	1·8	10·9	10·00	0·6	nil	NN
	C–34	12–24	0	6·30	6·40	40·5	1·847	1·6	8·7	8·88	0·5	nil	NN
	C–35	24–36	0	6·20	6·40	52·5	1·515	—	nil	11·20	0·2	nil	NN
	C–36	36–48	0	6·40	6·40	60·8	1·683	1·9	11·3	10·40	0·6	nil	NN
8	C–2893	0–12	0	7·30	7·80	40·0	1·377	7·6	55·1	8·56	3·8	traces	N
	C–2894	12–24	0	7·20	7·60	47·6	1·262	4·8	38·1	11·04	2·8	nil	N
	C–2895	24–36	0	7·10	7·60	41·5	1·262	3·0	23·8	8·00	1·4	nil	N
	C–2896	36–48	+	8·60	9·40	59·4	1·377	6·3	45·7	16·00	4·0	nil	N
9	C–231	0–12	+ +	9·30	9·70	37·2	1·515	10·1	66·5	6·96	7·0	nil	N
	C–232	12–24	+ +	9·00	9·60	55·3	4·208	34·9	82·9	8·48	16·00	nil	SA
	C–233	24–36	+ +	9·20	9·60	48·7	3·987	27·4	68·7	8·40	11·0	nil	approaching S
	C–234	36–48	+	8·90	9·50	56·3	3·833	25·8	67·4	10·08	11·0	traces	approaching S

0 = non-calcareous; + = slightly calcareous; + + = moderately calcareous; + + + = highly calcareous; N = normal; S = saline; SA = saline alkali; NSA = non-saline alkali

possible future danger from accumulation of salts. The top layer of the latter profile has a high pH value and a high soluble-sodium percentage, but its present salinity status does not appear to be harmful. This top layer, however, rests on subsoils which are already saline-alkali or saline in nature. The saturation extract of the second layer has a conductivity slightly above 4 millimhos/cm. and an exchangeable-sodium percentage above 15, giving it the characteristics of a saline-alkali soil. The succeeding two layers approach the conditions of a saline soil, showing a high conductivity and lower exchangeable sodium. These conditions have been caused primarily by bad internal drainage in the soil profile since such types of land occur as low-lying pockets in areas of flat topography where soil salinity may arise.

TABLE 3

Composition of the Saturation Extracts—Surface Soils

Profile No.	Lab. No.	Depth (in.)	Conductivity (millimhos/cm.)	Cations m.e./litre				Anions m.e./litre				
				Ca	Mg	K	Na	CO_3	HCO_3	Cl	SO_4	NO_3
1	C-1992	0–18	1·010	3·0	1·0	0·3	5·1	0·0	5·0	6·0	0·0	0·0
2	C-1942	0–12	13·528	3·5	1·0	1·5	145·3	90·0	51·0	8·0	0·0	traces
3	C-753	0–12	16·834	8·0	3·0	0·8	155·9	142·0	13·0	14·0	0·0	traces
4	C-2238	0–18	5·611	4·5	2·0	1·5	48·8	0·0	42·0	15·0	0·0	traces
5	C-1865	0–10	2·913	6·6	3·3	traces	21·9	0·0	19·4	10·0	0·0	0·0
6	C-2067	0–9	2·913	2·0	0·5	traces	27·1	0·0	18·0	10·0	0·0	0·0
7	C-33	0–12	1·646	7·5	11·0	1·1	1·8	0·0	10·5	10·0	0·0	0·9
8	C-2893	0–12	1·377	4·0	3·0	0·6	7·6	0·0	8·0	5·0	0·0	0·0
9	C-231	0–12	1·515	3·5	3·0	0·3	10·1	0·0	6·0	11·0	0·0	0·0

Discussion and Summary

Soils from some of the areas lying in the Indian Gangetic alluvium in the central and north-western portions of the State of Uttar Pradesh have been rendered uncultivable due to the accumulation of salts and consequent soil salinity and alkali. The main factors responsible for salinization of these soils are the arid climate and poor internal drainage. Irrigation waters do not appear to be a primary source of salts since it is known that these areas have never received irrigation in the past. The main source of soluble salts in these soils seems to be the weathering of minerals, either *in situ* or elsewhere, and subsequent transport and accumulation with ground waters. Saline and alkali soils in this state, therefore, occur topographically in low-lying pockets where the ground water is high or there is poor internal drainage. Restriction in drainage in the profile is caused by the presence of either an indurated clay-pan or in more mature formations by a cemented lime-carbonate nodule (*kankar*) pan with or without a high ground-water table.

These soils are characterized by very high pH values and almost complete absence of gypsum. It is in these essential features that the soils reported in this paper differ fundamentally from some similar soils in other parts of the world. The high pH values have been caused presumably by the much higher temperatures prevailing in the tropics and the alternate annual wetting and drying of the soils as a result of the

monsoonic climates, promoting rapid hydrolysis of the sodium soil complex. No relationship has, however, been found between the exchangeable-sodium content and the change of pH values with dilution of the soil suspensions. But this behaviour is in conformity with that reported by Richards (1950) for American saline and alkali soils. The absence of gypsum in the profiles of the Indian saline and alkali soils of alluvial origin is due to the higher rainfall (30 to 35 in. per annum) under which these soils have developed. Although in place of gypsum a zone of accumulation of $CaCO_3$ can be encountered in these soils, this lime is always present in the form of nodules and is in fact the $CaCO_3$-illuviation horizon of the saline-alkali soils. In practice, therefore, such soils cannot be reclaimed by the mere process of leaching even on improving internal drainage, as in the absence of gypsum there is no readily available source of soluble calcium compounds for exchange reactions in the soils themselves. Nodular $CaCO_3$ is known to be extremely stable and slow in producing soluble calcium ions in the soil solutions unless a fairly high CO_2 concentration is maintained in the soil or an acidifying chemical amendment is used in the process of reclamation.

The composition of the saturation extracts from the surface soils shows that the contents of sodium ions are unusually high as compared with calcium and magnesium ions. This factor is responsible for high pH values of the soil suspensions. Since the presence of carbonates amongst the anions is found only for those soils in which the contents of sodium is over 90 per cent., the carbonates get precipitated along with calcium and magnesium in the process of the preparation of saturation extracts in cases where the concentration of monovalents is not so high. The pH values of the more dilute 1 : 2·5 or 1 : 10 soil-water ratios, therefore, continue to show higher figures indicating the presence of carbonates in such suspensions. The complete absence of sulphates in the anions of the saturation extracts is in agreement with the insignificant quantities of gypsum detected in the soils. Nitrates are found only in traces and only in some of the soils with high sodium contents. The soils, accordingly, appear to be the carbonate-chloride type of saline-alkali soils, in contrast to soils of more arid localities of temperate climates where the sulphate-chloride type of formation may be the predominant class.

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(*Received 11 May 1953*)